Pitting Corrosion on Sulphide Inclusions in Stainless Steel 316

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Summary

Pits have been observed to initiate at certain inclusions in stainless steel, which affect the composition and properties of the passive film in that region.

In this thesis, the VG MA500 high resolution scanning Auger microscope associated with Link EDX is used to investigate the surface chemistry of inclusion groups in stainless steel 316 relative to the bulk composition, before and after exposure to sodium chloride solution. The work demonstrates that careful control of experimental conditions allows the progress of initiation of pits to be observed systematically. The role of inclusions as initiators of pitting corrosion has been studied from the very inception of attack. Detailed observation have been taken from separate manganese sulphide as well as mixture of manganese sulphide and multi-element oxide at various pH values of solutions to trace the behaviour of these inclusions during exposures.

It is suggested from this investigation that corrosive attack starts on MnS inclusion proper. The dissolution of MnS takes place in sodium chloride solution followed by the acidification in the microarea and dissolution of metal in the region adjacent to the inclusion. The mechanism for the crevice corrosion is of importance after the microcrevice forms. The observations showed that sulphur precipitated on the area surrounding the inclusion group in acidic sodium chloride solution. This is in contrast to the finding in prior studies by electron probe or EDX analyses in which sulphur precipitation was only observed on the inclusion. Because pitting normally occurs on surfaces that are initially exposed to air before being immersed in the corrosive solution, an understanding of
the change of surface film associated with the change of medium is very important. XPS was used in this work to study the air formed and aqueous films, the transformation when the specimens were immersed in solutions.

The study of the energy-loss structure of photoelectron peaks has lead to a better understanding of these various films. It has been used to study in greater detail the composition and properties of the films formed on Fe-Cr alloys during oxidation, vacuum annealing, and to find the relationship between the depth distribution of the components in the films and energy loss background of photoelectron peaks. Three features are of particular importance: the background loss tail height, the baseline slope and the post-peak loss structure. These features have been related quantitatively to the relative amounts of the element and the surrounding matrix in the layers which contribute the greatest signal at any given take-off angle. The present work illustrates that the additional depth information available from closer inspection of the inelastic loss background feature may aid an understanding of the change from the air-formed film to the aqueous film as well its effect on the initiation of pits in stainless steel 316.

The combination of AES and EDX with high spatial resolution gave an opportunity to re-investigate the initiation of pits at the site of inclusion on stainless steel by offering both bulk and surface information.

The use of AES and XPS associated with the energy loss structure of photoelectron peaks facilitates a comprehensive understanding for the whole surface of various films and the local areas which are involved in the formation of pits.
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Chapter 1

Introduction

Pitting corrosion has been under investigation for more than fifty years, mainly using electrochemical techniques and electron microscopy. Pits on 'stainless steel' have been observed to initiate at certain inclusions, which affect the composition and properties of the passive film. During the last 20 years, great attention has been devoted to the importance of sulphide inclusions for the initiation of such localized corrosion. The use of electron microprobe analysis has been of special importance for the determination of the composition of inclusions and steel matrix. However, because of the small dimensions of pits and their apparent occurrence at unpredictable points on the surface, it has not yet been possible to study the reasons for the initiation of an individual given pit. Surface analytical techniques have now been improved to such an extent that studies can be performed in the micro region on passive surfaces, on the sites of developing pits as well as the surrounding areas. High resolution Auger analysis enables us to locate clusters of specific elements on the surface of inclusions and the surrounding area.

To investigate the initiation of pits, it is also very important to understand the formation and transformation of the passive film under differing conditions. When the specimen, which possesses an air-formed passive film and some inclusion particles on the surface, is exposed to corrosive solution, the air-formed passive film will change to an
aqueous oxide film; the inclusion may be dissolved and a pit may form in the site of inclusion.

Using the combination of XPS and high resolution AES and EDX, it will be possible to build up a complete picture of the behaviour of passive films and inclusions. XPS is used to study the surface composition and chemistry of films. Associated with ion sputtering and angular resolved electron spectroscopy, XPS can contribute to our knowledge of these films. High spatial resolution, scanning AES and EDX are used to study the area where there are inclusions and pits, and to follow their changes as the specimen is exposed to corrosive solution. The MA500 scanning Auger microscope is equipped for such simultaneous collection of Auger and X-ray spectra or maps. It thus works in two depth planes -- AES for surface information; EDX for bulk information.

To understand the depth distribution of elements in the near surface region of the passive film, the additional in-depth information obtainable from the energy loss feature of photoelectron peaks is used together with that obtained by the traditional means, angular XPS and ion sputtering.

In this thesis the above range of advanced analytical techniques have been used to study the onset of pitting at inclusions when the steel is exposed to chloride solutions. It is expected that these might make for an understanding of specific cases of corrosion under more industrial relevant conditions.
Chapter 2

Literature Survey

2.1 Corrosion Properties of Stainless Steel

The broad classification of corrosion reactions into 'wet' or 'dry' is generally accepted and the terms are in common use. The term 'wet' includes all reactions in which an aqueous solution is involved in the reaction mechanism; implicit in the term 'dry' is the absence of water or an aqueous solution.

In both 'wet' and 'dry' corrosion, transport of ions are important. However, the transport properties of the solid and the aqueous electrolyte are very different. Thus, in 'wet' corrosion, the oxidation of the metal and reduction of a species in solution (electron acceptor or oxidising agent) may occur at different areas on the metal surface whereas this does not occur in gaseous oxidation (1).

The study of corrosion is essentially the study of the nature of the metal reaction products and of their influence on the reaction rate. The behaviour of metals and alloys in most practical environments is highly dependent on the solubility, structure, thickness, and adhesion of the solid metal compounds that form during a corrosion reaction. These may be formed naturally by reaction with their environment (during processing of the metal and/or during subsequent exposure) or as a result of some deliberate pretreatment process that is used to produce thicker films or to modify the nature of existing films. The importance of these solid
reaction product is due to the fact that they frequently form a kinetic barrier that isolates the metal from its environment and thus control the rate of the reaction; the protection afforded to the metal depends on the physical and chemical properties outlined above (2).

2.1.1 Composition of the Passive Film

The useful corrosion resistance of a stainless steel is due almost entirely to the fact that it exhibits passivity in a wide range of environments. Faraday suggested that passivation is caused by an invisible oxide film on the metal surface, or by an oxidised state of the surface, that prevents contact between the metal and the solution.

Stainless steels, easily passivated because both their air-formed oxide films and anodically formed oxide (containing Cr$^{+3}$), are 'stronger' and stable at more negative potentials than the corresponding films on iron, so are even more easily maintained passive (3). The existence of passive oxide films on stainless steels has been demonstrated by Evans and Stockwell (4), Vernon et al (5), Mahla and Nielsen (6) and Rhodin and Nielsen (7). The oxide-film theory in its modern form, due primarily to Evans (8), has been supported and extended with modifications of detail, by the great weight of qualitative evidence and quantitative measurements. The films have also been analysed chemically by electron spectroscopy. The thin transparent film comprises only a few molecular layers, in the approximate thickness range 1-10 nm.

As the system change from the active to the passive state the initial interaction depends on the composition of the aqueous phase. An initial chemisorbed state on Fe, Cr, and Ni has been postulated in which the
adsorbed oxygen is abstracted from the water molecules (9). With increase in anodic potential a distinct 'phase' oxide or other film substance emerges at thicknesses of 1-4 nm (2).

In near-neutral solution the passive film on Fe (2-6 nm thick) has been characterised as the so-called cubic oxide \( \gamma-\text{Fe}_3\text{O}_4 \) overlaying a thin film of \( \text{Fe}_3\text{O}_4 \) on the metal surface (10). The spinel structure derived from magnetite is prominent. Its structure is considered to be cation defective with protons (\( \text{H}^+ \)) progressively replacing \( \text{Fe}^{2+} \) in the \( \text{Fe}_3\text{O}_4 \) spinel, and leading to a continuous series of solid solutions of which \( \text{Fe}_3\text{O}_4 \) and \( \text{Fe}_2\text{O}_3 \) are the end products. Water is incorporated into the passive film by a process of oxidative hydrolysis of the initial \( \text{Fe}_3\text{O}_4 \) substrate as the potential of the metal is progressively raised.

An important feature of such films is their low ionic conductivity that restricts cation transport through the film substance and hence reduces further film growth. At elevated anodic potentials, adsorption and entry of anions, particularly chloride ions, may lead to instability and breakdown of these protective films (2, 3, 11).

The passive films formed on austenitic and ferritic stainless steel have been found to be enriched in chromium (12-15). Hashimoto et al (14) reported that Cr exists as a hydrated chromium oxy-hydroxide. Olefjord et al (15) suggested the films consist mainly of chromium oxide and hydroxide. Their XPS results on passive films of stainless steels show that Mo is enriched in the passive film, which is consistent with that of Sugimoto and Sawada (16) who found that the Mo content of the films increases almost linearly with the increase of Mo content in the bulk alloy. Hashimoto et al (14), however, have analysed the passive films of 19Cr-2Mo and 19Cr
ferritic stainless steel, formed by polarization in 1N HCl, by using XPS and reported that the composition of the passive films of both steels is nearly the same and that very little Mo was found on 19Cr-2Mo stainless steel. The AES results of Lumsden and Staehle (12), Cahoon and Bandy (13) also reported very little Mo in the passive films of stainless steels.

When iron itself is passivated, e.g. in borate buffer solution, Auger spectroscopy (Seo et al (17)) indicated that the film formed has two layers: the outer region differed in iron/oxygen ratio and contained elements from the passivating bath; the inner layer was free of other ions and corresponded in composition to Fe₂O₃. It has been suggested that the outer layer is formed by solution phase transport and deposition whilst the inner layer is formed by direct oxidation at the metal surface. The XPS measurement of Komo and Nagayama (18) showed the outer layer to be highly hydrated FeOOH.

The passive film not only consists of oxide of iron, chromium and some nickel and molybdenum, but also contains bound water. As a result of their analysis of desorption rates in dioxane solvent, Okamoto and Shibata (19) suggested that there exist two kinds of bound water in the film on passivated 304 stainless steel. They also assumed that the passive film was composed mainly of polymeric hydrous metallic oxides. At any stage of passivation, the passive film probably includes various forms of bridges between metal ions, e.g. M-H₂O-M, M-OH-M, M-O-M, depending on the degree of deprotonation.

The analysis of ESCA results from a series of Fe-Cr alloys by Sugimoto et al (20) indicated that oxygen in the film was present in two different binding states, one of which was identified as M-OH or M-O-OH type bonds,
and the other attributed to M-O type bond. The latter type of oxygen seems to be combined more firmly to the metal ions compared with the M-OH type oxygen. They found that the M-OH type oxygen decreased with increasing passivation potential. Such behaviour of oxygen is confirmed again by Hashimoto et al (21) who developed a sophisticated method which was able to determine the thickness as well as the composition of the passive film formed on alloys using ESCA.

H. Saito et al (22) suggested that the two kinds of bound water have a different inhibitive action against the attacks of chloride ions. The first kind of bound water consists mainly of aquo and hydroxyl groups, which could be replaced easily by chloride ions, as well as a few olation bridges. This bound water acts as an effective species to capture the released metal ions, the resultant hydroxylated metallic ions, MOH\(^+\) contributing to repair the film. The second kind of bound water, which is extracted with difficulty by dioxane, probably consists of olation and oxolation bridges between metal ions. This kind of bound water increases the film resistivity against attack by chloride ions due to its strong bounding to metal ions, but has less ability to promote self-repair, so that the breakdown of the film is accelerated once a pit nucleates. The authors suggested also that the first kind of bound water can be transformed into the second kind of bound water at higher passivation temperatures and longer passivation times, but the reverse process of the transformation is impossible.

2.1.2 Effects of Alloying Elements
It has long been known that the structure of stainless steel (ferritic, martensitic, austenitic) establishes its basic physical properties.

Fig 2.1 proposed by Schaeffler (23) indicates the effect of composition on the structure of material after rapid cooling to room temperature from a temperature of 1050°C. The other alloying elements used in steel manufacture exhibit the same effect as either chromium or nickel, although to different extents. The corrosion behaviour of metal, such as the pitting potential is strongly affected by alloying elements. The general form of the anodic polarization curve of stainless steels in acid solutions as determined potentiostatically or potentiodynamically is shown in Fig 2.2.1 (23), curve ABCDE. If the cathodic curve of the system PQ intersects this curve only at a point P between B and C, the steel is passive and the film should heal even if damaged. This represents a condition in which the steel can be used with safety. If, however, the cathodic curve P'Q' also intersects the section ED the passivity is unstable and any break in the film would lead to rapid metal solution, since the potential is now in the active region and the intersection at Q' gives the stable corrosion potential and corrosion current.

The relative effects of some of the alloying elements utilised may be gauged from the potential and current density figures for several standard steels shown in Table 2.1 (23). Increasing chromium content depresses the potential C, therefore extending the range of stable passivity, but it also increases the critical current (at point D) so that higher corrosion rates are obtained in the absence of passivity. Nickel also depresses potential C but markedly reduced the critical current. Molybdenum also has beneficial effects on both breakdown potential and critical current.

In near neutral or alkaline salt solution, anodic polarization curves
Fig. 2.1 Structure of steels after cooling from elevated temperature as determined by composition. A austenite, M martensite and F ferrite (after Schaeffler, Truman, (23))

Table 2.1.0 Composition of steels which are listed in Tables 2.1.1 and 2.1.2 (After Truman, (23))

<table>
<thead>
<tr>
<th>Steel number</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>410S21</td>
<td>0.09-</td>
<td>11.5-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>431S29</td>
<td>0.12-</td>
<td>15.0-</td>
<td>2.0-</td>
<td></td>
</tr>
<tr>
<td>430S15</td>
<td>0.10 max</td>
<td>16.0-18.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>434S19</td>
<td>0.10 max</td>
<td>16.0-18.0</td>
<td>0.90-1.30</td>
<td></td>
</tr>
<tr>
<td>304S16</td>
<td>0.06</td>
<td>17.5-</td>
<td>9.0-</td>
<td></td>
</tr>
<tr>
<td>316S16</td>
<td>0.07</td>
<td>16.5-</td>
<td>9.0-</td>
<td>1.25-</td>
</tr>
<tr>
<td>317S16</td>
<td>0.06</td>
<td>17.5-</td>
<td>12.0-</td>
<td>3.0-</td>
</tr>
</tbody>
</table>
Fig. 2.2.1 Idealised form of a potentiostatic anodic polarisation curve ABCDE for stainless steels as determined in sulphuric acid solution. PQ and PQ' are two cathodic polarisation curves that lead to passivity and corrosion, respectively (after Truman, (23)).

Table 2.1.1 Some critical values from anodic polarisation curves determined potentiodynamically in 20% sulphuric acid at 27°C (see Fig. 2.2.1) (after Truman, (23)).

<table>
<thead>
<tr>
<th>Steel</th>
<th>Potential* C (V)</th>
<th>Potential* E (V)</th>
<th>Critical current density D (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>410S21</td>
<td>+0.17</td>
<td>-0.42</td>
<td>50</td>
</tr>
<tr>
<td>431S29</td>
<td>-0.02</td>
<td>-0.42</td>
<td>12</td>
</tr>
<tr>
<td>430S15</td>
<td>-0.20</td>
<td>-0.55</td>
<td>100</td>
</tr>
<tr>
<td>434S19</td>
<td>-0.25</td>
<td>-0.55</td>
<td>15</td>
</tr>
<tr>
<td>304S16</td>
<td>-0.25</td>
<td>-0.37</td>
<td>0.15</td>
</tr>
<tr>
<td>316S16</td>
<td>No breakdown under test conditions used</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Versus S.C.E
Fig. 2.2.2 Idealised form of a potentiostatic anodic polarisation curve for stainless steels as determined in a neutral solution containing chloride (after Truman (23))

Table 2.1.1 Breakdown potentials for various stainless steels determined potentiodynamically in 0.1M NaCl + 0.1M NaHCO₃ solution (Point B in Fig 2.2.2) (after Truman (23))

<table>
<thead>
<tr>
<th>Steel</th>
<th>Breakdown potential (V, vs S.C.E.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>410S21</td>
<td>-0.22</td>
</tr>
<tr>
<td>430S25</td>
<td>-0.12</td>
</tr>
<tr>
<td>431S29</td>
<td>-0.12</td>
</tr>
<tr>
<td>434S19</td>
<td>-0.08</td>
</tr>
<tr>
<td>Precipitation hardening</td>
<td>-0.08</td>
</tr>
<tr>
<td>304S16</td>
<td>-0.07</td>
</tr>
<tr>
<td>315S16</td>
<td>0.00</td>
</tr>
<tr>
<td>316S16</td>
<td>+0.14</td>
</tr>
<tr>
<td>317S16</td>
<td>+0.30</td>
</tr>
</tbody>
</table>
of the type shown in Fig 2.2.2 are obtained, in which the active loop CDE of Fig 2.2.1 is no longer apparent. At high potentials curve B'A' will represent oxygen evolution, but at low potentials (curve BA) in the presence of halide ions it is indicative of pitting corrosion. Breakdown potentials for various alloys are given in Table 2.1.2, and it can be seen that increasing chromium, nickel and molybdenum contents all lead to improved resistance to pitting, which is indicated by the magnitude of the breakdown potential.

The effects of alloying elements have been extensively studied for stainless steels, and have been reviewed by various authors (24-27). It is known that V, Cr, Ni, Mo, W, Re, Ag, Si and N increase the pitting potential of stainless steels in chloride-containing solutions. On the other hand, alloying elements such as Ti, Co, Mn, Se, Te, S, Gd and Ce were found to be detrimental; Cu, B, and C give variable effects depend on their quantity and the phase present.

Chromium constantly has been observed to be a beneficial alloying element. Auger spectroscopy showed that Cr was greatly enriched in the film whereas nickel was apparently excluded from it (28). Because of its better pitting resistance compared with iron which is the main constituent of the surface film, the enrichment of chromium in the film tends to make the film have greater resistance to pitting.

As is well known molybdenum improves the resistance of austenitic steel to crevice and pitting corrosion. The critical current density for passivity decreases sharply at all Ni levels with the increase in Mo content (29). No clear consensus, however, has yet been reached on the role of molybdenum in steel. Lumsden and Staehle (28) concluded that
molybdenum was excluded from the film but enhanced the chromium enrichment and this finding was repeated by other workers using the AES technique. In the work of Hashimoto et al (30) on amorphous alloys, the chromium content of the film formed on the material including 2% Mo increased to 18% from 3% in the bulk alloy. It is frequently suggested that Mo and Cr are enriched together on active surfaces.

The investigation of Sugimoto et al (16) shows that:

(1) The presence of a certain amount of Cr is essential to increase the pitting resistance of steels in acid chloride solutions by Mo alloying;

(2) The passive films of the Mo-containing Cr-Ni steels consists of complex oxyhydroxide containing Cr$^{3+}$, Fe$^{3+}$, Ni$^{2+}$ and Mo$^{6+}$ ions. Mo($^{6+}$) oxide, which is contained in Cr($^{3+}$) oxyhydroxide in a state of solid solution, is suppressed from its transpassive dissolution and contributes to the remarkably increased resistance to attacks of Cl$^{-}$ and acids because of the natural stability of Mo($^{6+}$) oxide in acid solution;

(3) The thickness of the passive film of Cr-Ni steels increases with increase in Mo content both in H$_2$SO$_4$ and HCl solution.

Additions of Mo to austenitic Cr-Ni stainless steels, give a marked improvement in the resistance to chloride pitting, which has also been reported by many other authors (31-40). Molybdenum is effective as a pitting inhibitor in the presence of chromium (41). In the absence of chromium, however, the presence of Mo had almost no effect on the pitting potential, as shown by Stout et al (42) for binary Fe-Mo alloys.

Nitrogen strongly increases the pitting potential of austenitic stainless steels in chloride solutions. Osozawa et al (43) reported measurements on stainless steels containing from 0.02-0.2% N and 16-25 wt% Cr. The stainless steel tested in 4% NaCl solution showed a shift in
pitting potential towards more the noble direction with an increasing amount of nitrogen. They concluded that nitrogen acted by consuming protons in the depassivated sites, producing ammonium ions, and thus prevented the lowering of pH before the sites could grow as ordinary pits. To develop an economical corrosion resistant austenitic steel, the effects of N as a substitute for Ni were investigated by Sakamoto et al. As much as 0.35% N is soluble in 25% Cr steel and works as an austenitic former approximately 30 times stronger then Ni. Nitrogen in austenitic stainless steel improves the resistance to pitting corrosion and to strong acids.

Some alloying elements act in combination with others. Among the numerous alloying elements, chromium is the most important one. The importance of chromium to passivation was studied by Hashimoto et al (30). The metalloid additions of P, C, Si, B to an iron 10% chromium alloy change the corrosion rate of the passive films formed in 0.1N sulphuric acid to different extents. XPS analysis showed that the difference of corrosion rate is caused by different Cr(+3) content in the oxide passivating film, see Fig 2.3 (30, 45). XPS has shown that, instead of forming an important constituent of the film, these elements appear to function by stimulating the active dissolution of iron which leads to the enrichment of chromium.
Fig. 2.3 Concentration of Cr in passive film (at%) (after Hashimoto et al, Castle, (3)(45))

Fig 2.4 Surface oxides on Fe-Cr alloys (after Grimley, (62))
2.2 The Oxidation of Iron/Chromium Alloys

When a solid metal is attacked by oxygen gas, the product of the reaction is the metal oxide which, if it is not volatile, builds up as a surface layer on the metal. The oxide layer may be protective or non-protective. The nature and thickness of the oxide film depend on many factors including temperature, the nature of the atmosphere and its partial pressure of oxygen, and the physical metallurgy of the metal (46, 47).

Thermodynamics may be useful to predict the composition of an oxide formed on alloys, although oxidation processes are not normally equilibrium processes. The rate of growth of the oxide is governed by kinetics and different empirical rate laws will be followed.

When a non-protective layer does not inhibit the continued access of oxygen to the unchanged metal, the law of growth is

\[
\frac{dX}{dt} = k_1 \quad (2-1)
\]

or

\[
X - X_0 = k_1 t \quad (2-2)
\]

where \( X \) the thickness of film
\( k_1 \) the linear rate constant

When a protective oxide layer forms a continuous barrier between the reactants (oxygen and metal), which inhibits the reaction, the simplest assumption that can be made about the effectiveness of this barrier is that its protecting power is directly proportional to its thickness. Then

\[
\frac{dX}{dt} = k_2 / X \quad (2-3)
\]

or

\[
X^2 - X_0^2 = 2k_2 t \quad (2-4)
\]

where \( k_2 \) the parabolic rate constant.

This law is obeyed for the high-temperature oxidation of many metals. For the case of low temperature (such as below room temperature to
approximately 400°C), this simple relationship is not found and logarithmic and inverse logarithmic laws are generally obeyed, i.e.

\[ \frac{dX}{dt} = k / e^x \quad (2-5) \]

or \[ X = a \ln(1 + kt) \quad (2-6) \]

This review first examines the oxidation of iron which is the base material for the majority of alloys, and then covers iron-chromium alloys which are used in the present work.

Because iron is a base material for the majority of alloys, the oxidation of iron has been extensively studied, and most experimenters agree upon the nature and formation of oxides on pure iron (46, 48-56). The mechanism for growth is by the outwards diffusion of iron to the surface through the oxide. On the surface, the iron cations react with the oxygen. As mentioned above, the parabolic rate law is obeyed at temperature greater than about 400°C (48) and the logarithmic rate law is obeyed at lower temperatures (46).

Many studies have been made of the oxidation behaviour of polycrystalline and single-crystal Fe at temperatures at and below 350°C, both in air and in O₂ at pressures from 0.01 to 760 Torr (57). It has been shown that the overall thickness, adherence, and, in particular, relative amounts of the different Fe oxides are a function of the Fe purity, specimen pretreatment, and oxidation conditions. In general, at temperatures below 175°C, the oxide film is cubic, whereas at higher temperatures up to and including 350°C, α-Fe₂O₃ is additionally formed.

Boggs et al. (58) studied the effects of crystallographic orientation
and oxygen pressure on the oxidation of iron, and found that a film of Fe$_3$O$_4$ forms rapidly on the surface when clean iron is exposed to oxygen at temperatures of 200°–400°C. Soon after this a second phase α-Fe$_2$O$_3$ begins to form in the outer surface of the Fe$_3$O$_4$ layer. The rates of nucleation and lateral growth of the second phase depend on the oxygen pressure and on the crystallographic orientation of the Fe$_3$O$_4$ matrix which is determined by the crystallographic orientation of the iron substrate.

A study has been made of the oxidation of (001) and (112) planes in Fe and polycrystalline Fe at 200°–320°C in 5x10$^{-3}$ Torr O$_2$ and the influence of substrate orientation and surface pretreatment were both found to be important.

The oxidation of iron-chromium alloys which form the basis for stainless steels, has been extensively studied. The formation of duplex scales on oxidized ferrous alloys, accompanied by segregation of the alloying elements, has been reported frequently in the literature.

Pfeil (59) showed that most of the transition elements with the exception of manganese, were concentrated within the inner layer of oxide formed on alloy steels in air at 1000°C. Moreau (60) reported that chromium concentrated in the inner scale on oxidized iron-chromium alloys, and Rahmel (61) found that vanadium, chromium, silicon and molybdenum were confined to the inner oxide scale of the respective binary iron alloys oxidized at 1000°C in oxygen. Grimley (62) assumed for simplicity that only FeO could be formed as the oxidation product of Fe on iron-chromium alloy. In addition, Cr$_2$O$_3$ and the spinel FeCr$_2$O$_4$ can be formed. By plotting dissociation pressure p against x$_{Cr}$ (Fig 2.4) he showed two critical Cr contents of the alloy. Below the first only FeO is formed,
between the first and the second only $\text{FeCr}_2\text{O}_4$ and above the second only $\text{Cr}_2\text{O}_3$. The existence of finite diffusion rates in the alloy will smear out these divisions, but the different zones are found. A $\text{Cr}_2\text{O}_3$ layer is normally protective and a spinel layer will be protective if the diffusion coefficient for $\text{Fe}^{3+}$ (or $\text{Fe}^{2+}$) in the spinel is lower than that in the oxides of iron. This protective layer (either $\text{Cr}_2\text{O}_3$ or $\text{FeCr}_2\text{O}_4$) is formed next to the alloy. Beyond this there will almost certainly be another layer composed mainly of the oxides of iron which is without influence on the protective properties of the alloy. The behaviour of the system is thus strongly dependent upon the chromium content, a level of 12% being the value which nominally separates stainless from non-stainless steels (63). A chromium content of 14% or more means that a chromia ($\text{Cr}_2\text{O}_3$) film will form, but this film will not reform once it has broken down — film healing requires a chromium content of around 18% (64).

Although experiments have shown that a variety of different films may be formed (47, 51, 65-72), the authors agree upon the underlying mechanism. Olefjord's (66) XPS studies of oxide films formed on austenitic stainless steel (18-10-1.8Mn) have shown that the composition of the films depends on the reaction temperature and time. At high temperatures, the oxide was found to be enriched with the easily oxidizable elements Cr and Mn. After oxidation at room temperature and at an intermediate temperature (250°C) iron was found to be the dominating component in the top layer of the oxide. Investigation of top layer after oxidation at 500°C for different times showed an increase of chromium content with oxidation time. The author further studied the composition profile of low temperature oxide formed on chromium steel in pure oxygen at 0.2 atm by using XPS and found that total chromium content in the oxide is proportional to the
concentration in the metal, but that it varies with depth inside the film. At the oxide-gas boundary the chromium concentration is less than in the metal, while chromium is enriched at the metal phase boundary. It is suggested that the oxide consists of \((\text{Fe, Cr})_2\text{O}_3\) in the outermost zone and \(\text{FeCr}_2\text{O}_4\) at the inside, with the reservation that the method is not sensitive to deviations from stoichiometry. The thickness of the layer has been determined as 25 Å from the intensity ratio of the deconvoluted XPS peaks of the metallic and oxidized states.

An air formed oxide may be partially or totally reduced when heated in a vacuum, so the composition of surface changes, but the final state of the metal surface may not necessarily be the same as the original condition since many of the diffusion processes are irreversible.

It has been demonstrated (73) that heating a specimen with a clean metallic surface in high vacuum \((10^{-9}\text{ Torr})\) results in a layer (or islands) of chromium oxide on the surface.

Asami et al (74) have studied the changes in the surface composition and thickness of a series Fe-Cr alloys when heated up to 380°C in a high vacuum by means of XPS. They found that remarkable enrichment of chromium occurs in surface film on the alloys containing 13% chromium or more. These changes are caused by decomposition of oxy-hydroxide-like structure, reduction of oxidized iron in the surface film and oxidation of chromium at the alloy surface. The iron is reduced either by active carbon or by the metallic chromium. At temperature lower than ca. 300°C, the change in the quantity of oxidized iron in the film depends not only on the composition but also on the structure of the film caused by the difference in initial surface treatment, although the other changes are essentially dependent on
the compositions of the surface film and substrate alloy. At temperatures higher than 300°C, the composition of the surface tends to $\text{Cr}_{2-x}\text{Fe}_x\text{O}_3$, where $x$ is nearly equal to zero for high chromium alloys at 380°C. The authors also found that the atomic fraction of chromium in the alloy surface just beneath the surface oxide film changes by heating. The decrease in the fraction of chromium appears to occur below about 300°C and increase above this temperature. This change in composition arises most intensely at the alloy composition of ca. 13 at% of chromium. They suggested this phenomenon is caused mainly by the balance of the consumption and supply of chromium by oxidation and diffusion and does not depend on the initial surface treatment which does not cause the change in the composition of the substrate alloy.

Several workers have also studied the oxidation and vacuum annealing behaviour of stainless steel (75-82). Leygraf et al (75-76) studied the interaction between (100) and (110) single crystals of Fe$_{0.84}$Cr$_{0.16}$ and oxygen gas in the pressure range $10^{-9}-10^{-7}$ Torr at room temperature and at 427°-627°C, using LEED and AES. They found that the interaction starts with a chromium-oxygen reaction next to the alloy surface, followed by an iron-oxygen reaction outside the chromium-oxygen layer. At 527°C these reactions are connected with redistribution of cations between the interior of the alloy and the surface region whereas at room temperature only a redistribution of cations within the surface region is observed. It is found that the formation of spinel-like oxide layer is favoured by lower values of the Cr/Fe surface ratio.

The type of oxide formed depends upon the rate of supply of metal ions and oxygen to the oxide/gas interface. If the supply of oxygen to this interface is matched by the chromium ion flux, a chromia film forms. If,
however, the supply of oxygen exceeds the chromium ion flux, iron (and nickel) oxides are able to form. Further more if the temperature is too high a chromium oxide film forms, but its growth is very rapid and results in the formation of a chromium depleted region beneath the scale, because the rate of chromium ion supply to the film exceeds the supply of chromium from the bulk to the subscale zone. If the oxides of a binary alloy are mutually insoluble, and if one of the components has a much greater affinity for oxygen than the other, then the oxide of the baser metal will be formed exclusively at low oxygen pressure even though it is present in the alloy in only a small amount (62).

Further, the investigation on thermal passivation of AISI 316 stainless steel in controlled vacuum, in the range 252°C–502°C (78) showed that independent of surface pretreatment the increase in critical potential for crevice corrosion in a neutral sodium chloride solution after thermal passivation is at least 250mV. Due to selective oxidation of chromium and nickel during such thermal treatments the beneficial effect in corrosion resistance is attributed to a marked chromium film enrichment and less-marked nickel film enrichment.
2.3 Pitting Corrosion on Stainless Steel

2.3.1 Localized Corrosion

All forms of corrosion that attack metal nonuniformly are included in a common term 'localized corrosion'. Under such conditions, certain areas of the metal surface corrode at higher rates than others due to heterogeneity in the metal, the environment or in the geometry of the structure as a whole (83).

Among the localized types of corrosion, are pitting, intergranular corrosion, crevice corrosion, stress corrosion, cracking, etc. The localization of the heterogeneity gives rise to different types of localized corrosion. Shreir (11) listed various types of heterogeneity and geometrical factors that lead to localized attack, as shown as Table 2.2, and emphasised that the examples must be regarded as general guidelines. Whether or not the heterogeneity leads to localized attack depends on the environmental conditions prevailing.

There is no general theory that explains all the forms of localized attack that occur with the variety of metal/environment systems encountered in practice. Nevertheless, many of the following factors play an important part in most forms of localized attack (11):

(1) The cathode/anode area relationship
(2) Differential aeration
(3) pH changes at the cathodic and anodic sites
(4) Corrosion products (film) present initially on the metal surface and those formed during the corrosion reaction.
Table 2.2 Heterogeneities that lead to localized attack*

(After L. L. Shreir)

<table>
<thead>
<tr>
<th>Heterogeneity</th>
<th>Area of metal that is predominantly anodic</th>
</tr>
</thead>
<tbody>
<tr>
<td>METAL AND METAL SURFACE</td>
<td></td>
</tr>
<tr>
<td>Differences in metallurgical structure</td>
<td>Grain boundaries, more reactive phases</td>
</tr>
<tr>
<td></td>
<td>(solid solutions, intermetallic compounds,</td>
</tr>
<tr>
<td></td>
<td>etc.,)</td>
</tr>
<tr>
<td>Differences in metallurgical condition due to thermal or mechanical treatment</td>
<td>Cold-worked areas adjacent to annealed</td>
</tr>
<tr>
<td></td>
<td>areas, metal subjected to external stress</td>
</tr>
<tr>
<td></td>
<td>anodic to unstressed metal</td>
</tr>
<tr>
<td>Discontinuities in conducting oxide film or scale or discontinuities in</td>
<td>Exposed area of substrate metal, in the</td>
</tr>
<tr>
<td>applied metallic coatings that are cathodic to the substrate</td>
<td>case of passive metals defects in the passive</td>
</tr>
<tr>
<td></td>
<td>film result in an active-passive cell with</td>
</tr>
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<td></td>
<td>intense localized attack on the active area</td>
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<tr>
<td>Crevices or deposits on a metal surface or any other geometrical</td>
<td>The area of the metal in contact with the</td>
</tr>
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<td>configuration that results in differences in the concentration of the</td>
<td>lower concentration of the cathode</td>
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<tr>
<td>cathodic reactant</td>
<td>reactant, although there are exceptions to</td>
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<td>Dissimilar metals in contact (bimetallic corrosion)</td>
<td>this rule</td>
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<td>The metal with the more negative corrosion</td>
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<td>prevailing (note that the standard electrode</td>
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<td>potentials are seldom applicable and the</td>
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<td>galvanic series can be misleading)</td>
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<td>ENVIRONMENT</td>
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<td>Differences in aeration or in the concentration of other cathode reactants</td>
<td>Metal area in contact with the lower</td>
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<td>Differences in temperature</td>
<td>Metal area in contact with the higher</td>
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<td>Differences in velocity</td>
<td>Metal in contact with solutions of higher</td>
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<tr>
<td>Differences in pH or salt concentration</td>
<td>Metal in contact with the solution of lower</td>
</tr>
<tr>
<td></td>
<td>pH or higher salt concentration</td>
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</table>

*The table provides a general indication of the area that is likely to be anodic, but it must be emphasised that there are many situations in which the heterogeneity will have no effect or where the converse to the above may occur.

A fundamental principle of corrosion is that the sum of the rates of the cathodic reactions must equal the sum of the rates of the anodic reactions, irrespective of whether the attack is uniform or localized:

\[
\sum I_a = \sum I_c \tag{2-7}
\]
where $I_a$ = the anodic current

$I_c$ = the cathodic current

If attack is uniform, and assuming that there is only a single predominantly anodic and cathodic reaction, then

$$\frac{I_a}{S_a} = \frac{I_c}{S_c} \quad \text{or} \quad i_a = i_c$$

(2-8)

since the area of the cathode $S_c$ equals the area of the anode $S_a$. On the other hand, if attack is localized $S_a < S_c$, and

$$i_a > i_c \quad \text{or} \quad \frac{i_a}{i_c} > 1$$

(2-9)

and the larger the ratio $i_a/i_c$, the more intense the attack. Thus localized attack usually involves a corrosion cell consisting of a large cathodic area and a small anodic area, and the effect becomes more pronounced the higher the rate of the cathodic process and the larger the effective area of the cathode.

In general, localized attack is more prevalent in near-neutral solutions in which dissolved oxygen is the cathode reactant; since in a strongly acid solution the millscale would be removed by reductive dissolution and attack would become uniform.

Localized attack can, however, occur on a surface of metal that is apparently uniform, and this occurs particularly with the highly passive metals that depend on a thin invisible protective film of oxide for their corrosion resistance. In such cases submicroscopic defects in the passive film may form the sites at which pits are initiated.

2.3.2 Pitting Corrosion on Stainless Steel

Pitting corrosion is a highly localized attack at specific areas resulting in small pits that penetrate into the metal and may lead to
perforation.

Stainless steels owe their good corrosion resistance to the presence of thin passive or protective surface film and may be susceptible to pitting attack when the surface film breaks down locally and does not reform. It is also observed that pitting is related to the presence of certain aggressive anions in the medium. The pitting of certain stainless steels occurs in solutions containing Cl\(^-\) ions, Br\(^-\) (but not I\(^-\) or F\(^-\)) ions, hypochlorite or thiosulphate anions. By contrast, pitting tends to be suppressed by the presence of oxyanions such as NO\(_3^-\) or SO\(_4^{2-}\) (11).

In general, pitting corrosion may be divided into two stages: pit initiation and pit propagation. During pit initiation the passive film breaks down and does not reform. During pit propagation, the small active sites formed in the initiation stage propagate, often very rapidly, to form pits (84).

2.3.2.1 Characteristic Electrochemical Parameters for Pitting

Galvele (85) has summarized characteristic electrochemical parameters for pitting. These include pitting potential, repassivation potential, inhibition and induction time.

(1) Pitting potential \( E_p \)

Electrochemical depassivation does not appear at any arbitrary potential value, but only above a certain potential called the pitting potential which is also referred to as the critical pitting or breakdown potential. Below this potential no pitting is observed, no matter how long it is subjected to experiment. Above this potential pitting would start after a short induction time in the cases of stainless steel. This
potential is a function of the composition of the medium, the temperature, the composition of the alloy, etc.

(2) Repassivation potential $E_r$

Another characteristic potential of the pitting process was described by Pourbaix (86) and it is known as the repassivation potential. Pourbaix reported that pits, which start to grow at a potential equal to or higher than the pitting potential, keep growing even when the potential is lowered below the pitting potential. The pits stop growing only when the potential is lower than a certain potential called the repassivation potential, or protection potential. Suzuki and Kitamura (87) have reported that the value of the repassivation potential is related to the degree of occlusion of the pit. It was also found that the difference between the pitting potential and the repassivation potential is a measure of the susceptibility of the metal to crevice corrosion (88).

(3) Inhibition potential $E_i$

Inhibition potential was first described for stainless steel in chloride solutions containing nitrates by Schwenk (89). It was found that, in these solutions above the pitting potential, pits were nucleated on stainless steel. By increasing the potential, the intensity of pitting increased but eventually a potential was reached above which the pits were repassivated. This potential was called the inhibition potential.

(4) Induction time $t$

The metal is passivated in the absence of the aggressive anions, and then, at a constant potential, the aggressive anions are injected into the solution, pitting does not start immediately. A certain induction time elapses before pitting initiation is detected.
Fig. 2.5 Definitions: (a) pitting potential: (b) repassivation potential (arrows indicate polarization direction): (c) inhibition potential: and (d) induction time (arrow indicates injection of aggressive anion solution) (after Galvele, 1978 (85))
Fig. 2.6 Chloride ion concentration within the pit as a function of its diameter: 1. slowly growing pits; 2. quickly growing pits. Pits grown on 18Cr-12Ni-2Mo-Ti austenitic stainless steel in 0.5N NaCl+0.1N H₂SO₄ solution, polarized to 0.86 V(NHE) at 20°C (Mankowski and Szklarska-Smialowska, 1975 (85,96))
The above electrochemical parameters related to a pitting process are schematically represented in Fig 2.5 by Galvele (85).

2.3.2.2 Experimental Approach of Pitting Corrosion

**Aggressive anions**

The presence of an aggressive anion is a necessary condition to start pitting. Galvele (85) listed a compilation of data of aggressive anions found in the literature and concluded that for metals forming highly insoluble oxides, only anions of strong acids are aggressive, while for those forming less stable oxides, anions of relatively weak acids can also produce pitting.

The same metal could show different pitting potentials in different anions, and the chloride ion is the most aggressive of all, since it shows the lowest pitting potential. The pitting potential, in general, decreases with the concentration of chloride ions, but increases with the concentration of inhibiting oxy-anions such as \( \text{OH}^-, \text{SO}_4^{2-}, \text{NO}_3^-, \text{CrO}_4^{2-}, \) etc. (11).

Uhlig et al (90, 91) have established the following relationships between \( E_p \) (V, VS, S.H.E) and \( a_{Cl} \) for Fe-18Cr-8Ni stainless steel

\[
E_p = -0.088 \log a_{Cl} + 0.168
\]  

(2-10)

They have also determined the minimum activity of inhibiting oxyanions \( a_{\text{Inh}} \) to inhibit the pitting of Fe-18Cr-8Ni stainless steel and found that equations of the type

\[
\log a_{Cl} = A \log a_{\text{Inh}} + B
\]  

(2-11)

are obeyed in which \( A \) and \( B \) are constants that depend on the metal and the nature of the inhibiting anions. The order of the effectiveness of
Oxyanions in inhibiting pitting for Fe-18Cr-8Ni was found to be as follows:

\[ \text{OH}^- > \text{NO}_3^- > \text{Ac}^- > \text{SO}_4^{2-} > \text{ClO}_4^- . \]

Simultaneously, they published diagrams where zones of occurrence of pitting and inhibition are shown.

The effect of pH appears to be controversial. For stainless steel it was found that the pitting potential was pH independent up to pH 8, but increased with the pH for higher pH values (90). The weak acid salts acted as pitting inhibitors for stainless steel.

Composition of solution inside the pit

The composition of the electrolyte inside the pit was different from that outside. A pH decrease in the solution inside artificial pits on aluminium has been reported by Edeleanu and Evans, Hagyard and Santhiapillai (92, 93). They also found that the chloride concentration inside the pit increased, reaching values about ten times higher than those in the bulk solution. Recent work on actual pits has shown that the solution inside those occluded corrosion cells has a lower pH and a higher ionic concentration than those of the bulk solution (94, 95). For stainless steels exposed to neutral 0.5M NaCl solution, the pH inside the pit was reported to be below 1.0 while the chloride concentration was 6.2M (95).

The composition of the solution inside the pit is a function of the pit size. Fig 2.6 (96) shows the chloride ion concentrations within the pits, which grew on 18Cr-12Ni-2Mo-Ti austenitic stainless steel in 0.5N NaCl + 0.1N H$_2$SO$_4$ solution, polarized to 0.86V (NHE) at 20°C, as a function of their diameters.
The effect of temperature on the pitting potential

The pitting potentials of stainless steels were found to decrease with an increase in temperature (97). The case is complicated by various factors. Kolotyrkin et al (98) reported a break in the curve of pitting potential versus temperature and this was related to a change in the sites for pitting. In the molybdenum-containing stainless steels the effect of temperature is quite complex. The addition of 2.4% Mo to a Fe-15Cr-13Ni alloy increases the pitting potential at room temperature from +0.28V (NHE) up to +0.73V (NHE). But the beneficial action of molybdenum is not the same at every temperature (99, 100).

2.3.2.3 Pitting Theories

Many pitting theories, very frequently conflicting and exclusive, have been proposed. The major source of confusion was related to the nature of passivity. Pitting being a process of passivity breakdown, any mechanism of pitting had to be related to some mechanism of passivity:

(1) Adsorption theory

This theory maintained that passivity was due to an adsorbed monolayer of oxygen. Uhlig and Gilman (101) and Kolotyrkin (102) explain the breakdown of passivity in terms of competitive adsorption between chloride ions in solution and the adsorbed monolayer of oxygen on the surface of metal.

According to Uhlig (101), although the metal has a greater affinity for oxygen than chloride ions, adsorption of the latter is favoured by an increase in the potential until a value is reached where the adsorbed oxygen at specific sites is replaced by chloride ions, which catalyse
anodic dissolution. Thus the induction period required for pitting, the
decrease in the pitting potential with increase in chloride ion
concentration and the increase when passivating anions are also present in
solution, are all explained in terms of competitive adsorption between
chloride ions and the adsorbed oxygen on the metal surface.

In the investigation of Strehblow et al (103), pitting potentials $E_p$
and inhibition potentials $E_i$ have been determined for iron and nickel for
different aggressive and inhibiting anions. The pitting potentials $E_p$ and
the inhibition potentials $E_i$ depend on the concentration of the aggressive
anions $A$ and the inhibitor $I$ according to the equations:

$$E_p = a + b \log [A] \quad (b < 0) \quad (2\text{-}12)$$
and $$E_i = a + b \log [A]/[I] \quad (b > 0) \quad (2\text{-}13)$$

The critical potentials are explained by the adsorption of aggressive
anions on the metal surface and their competition with the inhibitor.

(2) Solid film theory of passivity

The solid film theory claimed that passivity was due to the formation
of a three-dimensional oxide film on the metal surface. Partial or
complete breakdown of passivity, with the onset of corrosion, is brought
about by any factor that produces partial or complete removal of the
passivating film.

There is at present overwhelming information about the nature,
composition and thickness of the oxide films present on passive metals, so
it is accepted that the metal is initially covered by a three-dimensional
passivating oxide film.

Based on this assumption, Galvele (85) has tried to find out how such a
film is undermined by aggressive anions and to explain the existence of a
pitting potential, and its relation to the composition of the medium, the
alloy, etc. He summarized the mechanism of pitting as

Ion migration mechanisms

Flaws in the oxide film

Localized acidification mechanism.

The ion migration mechanism assumed that the oxide film was acting as a static barrier that isolated the metal from the solution. In order to initiate pitting under such condition, some reaction had to take place to bring the metal in contact with the aggressive ions of the solution. One possible way to initiate pits was for the aggressive ions to migrate into the passive film, thus contaminating it. Later, as a result of changes of the properties of the passive film, high currents could start to circulate through the contaminated zones, and pitting would start. McBee and Kruger (104) found that there were changes in the oxide film of Fe-Cr and Fe-Cr-Mo alloys, when exposed to chloride ions, although these changes were less pronounced than those found with iron. Nevertheless, it could not be confirmed that the observations made by McBee and Kruger were due to migration of chloride ions into the film. Szklarska-Smialowska et al (105) found, by studying with ESCA and Auger films on pure iron exposed to chloride-containing solution, that all the chloride was weakly bound to the surface of the oxide film, and that no penetration was detectable. No penetration was found either in the Fe-Cr or in the Fe-Cr-Mo alloys (106).

Wood et al (107) suggested that pitting starts at flaws present in the oxide film. Noise analysis of passive metal at constant potential either in the presence or in the absence of aggressive anions, suggests that in the passive film there is a dynamic balance between film rupture and selfrepair (108). The observation of Galvele et al (109, 110), however,
suggested that while flaw formation is a necessary condition for pit initiation, it is not a sufficient condition.

One of the earliest theories for the electrochemical depassivation type of pitting was one proposed by Hoar (111) who described the localized acidification mechanism and suggested that the 'activating' influence of chloride ion may be best explained, not by a selective adsorption of Cl\(^{-}\) as postulated by Kabanov (112), nor by the conception of high 'penetrating' power of Cl\(^{-}\) for the oxide films as argued by Britton and Evans, but by a consideration of influence of a non-depositing ion such as Cl\(^{-}\) on the pH of the electrolyte next to the anode. This acidification mechanism of Hoar (111) explained the pit propagation process, but could not explain pit initiation.

The first explanation for the existence of a pitting potential value with an acidification process was given for the pitting of copper in chloride-containing solutions by Van Muylder et al (114). Fig 2.7 shows schematic potential-pH diagram according to the pitting mechanism by Van Muylder et al (85, 114).

Assume that \(a\) is the pH of the bulk solution. Above the potential \(a\), the anodic reaction of the metal starts:

\[
\text{Me} + z(\text{H}_2\text{O}) = \text{Me(OH)}_z + z\text{H}^+ + z\text{e}
\]  

(2-14)

leading to localized acidification.

But if the electrode potential of the metal is lower than \(a\), any acidification leads the system to the immunity region of the E-pH diagram, where the metal is thermodynamically stable. Corrosion stops, and the localized acidification disappears by diffusion of the protons to the bulk solution. If, on the other hand, the electrode potential is above \(a\), the
Fig. 2.7 Schematic potential-pH diagram, a) pH of the bulk solution: \( a_1 \) - \( a_3 \), passive zone; \( a_2 \) pitting potential: b) pH of the locally acidified zone. According to the pitting mechanism by Van Muylder et al (1965) (after Galvele, (85,114))

Fig. 2.8 Unidirectional pit model (after Galvele, (85))
localized acidification could reach pH values of the order of b, and the potential is above $a_\infty$, the following reaction becomes thermodynamically possible:

$$\text{Me} = \text{Me}^{2+} + ze \quad (2-15)$$

soluble products are produced, and the corrosion reaction is not hindered by them. As for the acidification, it is perpetuated by the following equilibrium:

$$\text{Me}^{2+} + z\text{H}_2\text{O} = \text{Me(OH)}_z + z\text{H}^+ \quad (2-16)$$

which compensates for the loss of protons by diffusion or by reaction.

According to this mechanism, passivity of the metal by insoluble hydroxides or oxides, becomes thermodynamically unstable above the potential $a_\infty$. And the pitting potential, in neutral or alkaline solutions, is given by the equilibrium of equation (15). This thermodynamic mechanism succeeded in explaining the pitting potential of copper in chloride solutions, but not when applied to metals such as iron, aluminium, zinc etc, or when reducible anions such as nitrates were present in the solution. Neither did it explain the inhibition effect of buffer ions on the pitting process.

This mechanism was modified by Galvele and co-workers (109, 115-120). These authors introduced an electrochemical kinetic explanation for the pitting potential. The key point in the localized acidification mechanism is that there is a pH drop on the dissolving metal surface and that this pH drop is a necessary condition to sustain the pitting process. A unidirectional pit model was given and shown in Fig 2.8 (85). Further, the calculations were made for the ionic concentration diagrams of the following systems: Zn/Zn$^{2+}$, Fe/Fe$^{2+}$, Ni/Ni$^{2+}$, Al/Al$^{3+}$, Cr/Cr$^{3+}$ and Co/Co$^{2+}$, which shows the concentration of $\text{Me}^{n+}$, $\text{Me(OH)}^{(n-1)+}$ and $\text{H}^+$, as a function
of the product of the depth of pit x and the current density i in a unidirectional pit and proved that important acidification processes would take place at pit initiation. These ion concentration diagrams give a quantitative explanation of the influence of solution of pH, buffer ion, and inhibitors on the pitting potential and an explanation of the existence of a pitting repassivation potential, which is lower than the pitting potential. The inhibition potential can also be explained by the acidification mechanism for pitting.

By changing the external pH value of the boundary conditions in their calculations, Galvele et al evaluated the effect of pH on the pitting potential. Fig 2.9 shows the effect of the external pH on the concentration of H⁺ as a function of the product of the pit depth x and the current density i in a unidirectional iron pit (117). It is observed that by increasing the external pH values, the proton concentration curve is shifted to higher xi values. For a given x value, this means that with higher bulk solution pH values, higher current density values will be required to attain the same acidification. If the current density inside the pit is potential dependent, as is generally the case, this higher current density requirement will be reflected as higher pitting potential values. If the relation between potential and current density inside the pit follows a logarithmic law, the pitting potential should be expected to follow a law of the type

\[ E_p = A + b \log C_{\text{H}^+} \]  

(2-17)

where b is equal to the Tafel slope for the metal in the acid pit-like solution.
Fig. 2.9 Effect of the external pH on the concentration of $H^+$ as a function of the product of the depth $x$ and the current density $i$ in a unidirectional iron pit (after Galvele, (85))
2.4 Inclusions in Stainless Steel

The nucleation sites of pits have frequently been found to be related to microscopic features of the metal surface. For example, for stainless steels the location of the pits was usually found to be related to the presence of inclusions.

In the literature there exist many experimental data indicating that, in the case of materials of commercial purity, sulphide inclusions are the most susceptible sites for nucleation of corrosion pits (121). Both separate sulphide particles and complex sulphides occurring together with oxide inclusions could act as sources of localized attack (122-126).

2.4.1 Sulphide Inclusions — Pitting Attack on MnS Inclusions

The existence of inhomogeneous inclusions in or near a surface of metal makes the surface composition of that spot slightly different from the rest of the surface. In stainless steel, sulphur usually exists as sulphides, which form during solidification of steel, and these are predominantly manganese sulphide.

That localized corrosion of steel, particularly pitting, is initiated at sulphide inclusions was already known at the beginning of this century. Also as regards stainless steels there have long since been indications that pitting of these materials starts at sulphide inclusions (127-129).

Since sulphide inclusions exposed in the surface of a stainless steel are not coated with a passivating oxide film, gaps occur in the passive film, particularly in acid solution, exposing the active metal and giving rise to localized attack (130).
The sulphide inclusions have relatively high electronic conductivities compared to the surrounding oxide film and lower electronic conductivities than the stainless steel matrix. Therefore a potential difference exists between the sites of inclusions and the rest of the surface. In a radiochemical investigation on stress corrosion cracking in 304 stainless steel, Overman (131) suggested the preferential adsorption of anions Cl\(^-\) at the inclusion sites, which facilitate the pit nucleation process.

Wranglen (130) considered that sulphide inclusions are responsible for the initiation of attack in both carbon steels and stainless steels. In carbon steels, the attack starts in the matrix close to the sulphide inclusion which is more noble than the matrix. In stainless steel, the attack starts in the sulphide inclusion proper, which is less noble than the surrounding oxide films and then spreads to the active metal below the sulphide inclusions. The propagation of pits depends upon the formation of a concentration cell in which the pit solution has a higher salt content, a higher acid content and a lower oxygen content than the surrounding bulk of the solution. The author suggested a model on the initiation of pitting of stainless steels as Fig 2.10 (130).

In Wranglen's model, anodic dissolution of MnS forms elementary sulphur, and the electrode reaction takes place as
\[
\text{MnS} \rightarrow S + \text{Mn}^{2+} + 2e \quad (2-17)
\]
When a pit has reached certain depth, it has passed the initiation stage and enters the propagation stage.

Wranglen (130) also studied the propagation of corrosion pits, and suggested that the propagation of an established corrosion pit would seem
Fig 2.10(a) Schematic illustration of MnS inclusion in stainless steel, showing dimensions. Preferential adsorption of chloride ions occurs on the sulphide inclusion due to its higher electron conductivity, giving stronger electrostatic image forces than on the surrounding oxide film.

Fig. 2.10(b) First stage of the initiation of pitting on stainless steel: dissolution of the sulphide inclusion under the separation of elementary sulphur and the exposure of active, not oxide-coated steel along the periphery.

Anode reactions on sulphide:
1. MnS = S + Mn2+ 2e-
2. S + 3H2O = HSO4− + 5H+ + 4e−
3. HSO4− + H2O = SO42− + 3H+ + 2e−

Chemical dissolution of sulphide: MnS = 2H+ = H2S + Mn2+
Local cathode reaction: 2H+ + 2e− = H2

Fig. 2.10(c) Continued anodic attack on sulphide inclusion in stainless steel under oxidation to H2SO3 and H2SO4, which cause chemical dissolution of the sulphide. Incipient attack on the metal close to the inclusion (after Wranglen, (130))
Fig. 2.11 Schematic illustration of the electrochemical mechanism for the propagation of a corrosion pit in steel in neutral chloride solution, showing the autocatalytic, self-generating nature of pitting (after Wranglen, [130])
to be similar in both carbon steel and stainless steel. Fig 2.11 gives a schematic illustration of the electrochemical mechanism for the propagation of a corrosion pit in steel in neutral chloride solution, showing the autocatalytic, self-generating nature of pitting.

Eklund (132), however, observed discrete sulphur particles at the attacked areas and suggested that the particles were precipitated from the solution and gave a mechanism for the dissolution of MnS as follows:

\[
\begin{align*}
\text{MnS} + 4\text{H}_2\text{O} & \rightarrow \text{Mn}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e} \\
\text{Mns} + 2\text{H}^+ & \rightarrow \text{Mn}^{2+} + \text{H}_2\text{S} \\
\text{H}_2\text{S} & \rightarrow \text{S} + 2\text{H}^+ + 2\text{e}
\end{align*}
\]

(2-18) (2-19) (2-20)

Kolotyrkin et al (133) suggested that the preferential nucleation of pits on sulphide particles was due to a catalytic action of the sulphide ions.

Daud's (134) research suggested that the type of corrosion attacks on sulphide inclusions in stainless steel depends on the copper content of the inclusions. Pitting is likely to take place on pure MnS inclusion but not on copper enriched-MnS inclusions. He found that chloride ions are locally agglomerated on the surface of the pure manganese sulphide inclusions and result in an initial stage of attack at a micro-crevice at the sulphide and metallic matrix boundary. In contrast copper enriched-MnS inclusions showed no sign of micro-crevice and then the surface was uniformly corroded. The formation of copper sulphide is suggested to be important in reducing the amount of active species of sulphur on the corroded inclusions.

2.4.2 Oxide Inclusions
As mentioned above, the nucleation sites of pits have frequently been found to be related to the presence of inclusions — separate sulphide particles or complex sulphides occurring together with oxide inclusions.

Electron microprobe analysis (135) has shown that in single crystals of a high purity 16% Cr-Fe alloy the corrosion pits nucleated predominantly on the inclusions of chromium oxide which were the only kind of non-metallic inclusions present in the samples under investigation.

They suggested that the oxide inclusions can influence the pit formation simultaneously or independently in four different ways:

(1) Within the material investigated, there may exist some primary microcrevices between the inclusion and the matrix itself. At these sites pitting corrosion can nucleate in the same way as crevice corrosion.

(2) Because of the presence of oxide inclusions in the vicinity of the surface and the crevices between the inclusion and the matrix, a very irregular distribution of current density at regions of the inclusion may be expected. Thus in the neighbourhood of inclusions, the metal can dissolve at a relatively very high rate.

(3) In the neighbourhood of sites where inclusions or impurities are accumulated, regions of a different composition from the alloy matrix exist.

(4) In an oxidizing solution, where pitting corrosion is due to local cell action, oxide inclusions can influence pit formation by acting as local cathodes.

By electron microprobe investigation, Smialowski et al (136) studied the initiation of pits in a commercial austenitic 18%Cr-9%Ni steel and found the following non-metallic inclusions in steel samples under
investigation:

(1) Al, Mn and Cr mixed oxide in the form of particles up to 10μm diameter

(2) Mn and Fe mixed sulphides occurring either as separate particles or as shells surrounding the mixed oxide

(3) Very small (up to 1μm diameter) particles of oxides containing Si, Al, Mg and Cr, without sulphide shells

They suggested that in passive alloys the corrosion pits are preferentially nucleated at non-metallic inclusions. In this respect, the sulphide inclusions are particularly effective. In their presence, the oxide inclusions are practically inactive, but when no sulphide inclusions are present, the chromium oxide particles can nucleate the corrosion pitting.

The further study (137) on the surface of iron and stainless steel after anodic polarization in Cl−-containing borate buffer solutions suggests that distinct, discrete areas of strongly localized accumulation of chloride were observed on the metal surface after polarisation at potentials lower than the potential of pit nucleation. These areas occurred mainly at the boundaries between non-metallic inclusions and metal matrix.

The possible reasons why the most susceptible spots for local depassivation exist at the boundaries of the non-metallic inclusions have been discussed (121-123, 126, 135) and mentioned briefly above.

Due to the migration of ions in the electric field a considerable accumulation of aggressive ions is achieved first at those regions of the surface that dissolve at the highest rate. This creates conditions favouring the formation of a chloride salt layer at these sites. The salt
layer, in turn, would locally sustain a current density higher than that characteristic of the areas covered by the passive film. In this way, localized metal dissolution would be accelerated, resulting in the formation of pits. As well as the accumulation of Cl\textsuperscript{−} found at the boundaries of the inclusions. It therefore seems probably that pits develop first at sites where the Cl\textsuperscript{−} accumulation is greater, namely at non-metallic inclusions.

According to Kolotyrkin et al (98), at room temperature pits on stainless steels were nucleated on inclusions of mixed oxides that contained, besides oxygen, some two to four elements, such as silicon, calcium, and more rarely aluminium and magnesium. No titanium or manganese appeared in any of these inclusions. At 95°C, however, pits were nucleated on particles composed of many component oxy-sulphides, in addition to oxygen and sulphur. They contained at least five to seven elements, among which manganese and titanium were always present.
2.5 Objectives of This Investigation

As this review has shown, the nucleation sites of pits have frequently been found to be related to microscopic features of the metal surface. For stainless steels the location of pits was usually found to be related to the presence of inclusions. Information is still required on the effect of these inclusions on passive films, how the different inclusions nucleate pitting, and how the pitting propagation varies with time and change of corrosive environment. Since much of the work was undertaken before the introduction of modern, high resolution, micro analytical techniques, such as scanning Auger microscopy, it is possible that this information could be gained by a reinvestigation using such techniques. In this respect, the specific objectives of this work are to investigate:

(1) the composition and properties of the passive film in the inclusion areas and nearby regions;

(2) the behaviour of different kinds of inclusion when exposed in corrosive solution;

(3) the effect of solution composition.

The high spatial resolution and low beam currents of scanning Auger electron microscope permit identification of inclusion and pit areas by secondary electron image and measurement of the surface composition. The simultaneous acquisition of the X-ray signals excited by the electron beam from a given picture element can give the bulk analysis of inclusions and substrate alloy. The combination of both techniques is effectively an electron probe microanalyzer working in two depth planes and will form the major experimental method to achieve the above objectives.

Pitting normally occurs on surfaces that are initially exposed to air.
before being immersed in the working medium. It is intended that the investigation of pitting should include an understanding of the changes in the surface film associated with the change of medium.

A detailed study of XPS spectra using recent findings on the secondary features of the spectrum, such as energy-loss structure could lead to this better understanding and particularly a better understanding of the depth distribution of components.

This understanding is likely to be achieved by the pursuit of two further objectives:

(4) To study in greater detail the composition and properties of the oxide film formed on the iron-chromium alloy during oxidation and reduction.

(5) To find the relationship between the depth distribution of the component in the film and energy loss background of photoelectron peaks.

The combination of surface analysis by photoelectron spectroscopy, ion beam etching, and angular resolution techniques has provided a method capable of producing composition profiles of the thin oxide film formed on the alloy during oxidation / reduction. It is the aim of this investigation to confirm the information on the depth distribution obtained from electron spectroscopy by the extra information of the energy loss structure, and to show how deeper structures can be probed by the use of background intensities than by use of the peaks themselves. This may aid an understanding of the changes which occur when a steel is immersed in an aqueous environment after prior exposure to the atmosphere.
Surface Analysis

Corrosion necessarily involves a reaction of material with its environment at a solid-gas, solid-liquid or solid-solid interface. Although some stages of corrosion are not controlled by the rate of surface or interface reactions, surface reactions must occur in corrosion so that surface analytical methods are the principal tools to study these processes. The wide range of surface analytical techniques provide chemical and compositional information at the surface and/or interface that is not usually available by other methods.

In this investigation, techniques used include: X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and energy dispersive X-ray analysis (EDX).

3.1 X-ray Photoelectron Spectroscopy (XPS)

3.1.1 Introduction

XPS has its origins in the investigation of the photo-electric effect which was first reported by Hertz in 1887 (138). X-ray were used as the exciting photo source. The energy distribution of X-ray induced photoelectrons was studied as early as 1914 by Rawlinson and Robinson (139). In 1914, Rutherford (140) made a first attempt at stating the basic equation of XPS, which was subsequently modified to

\[ E_v = h\nu - E_b \]  \hspace{1cm} (3-1)
where $E_k$ is the kinetic energy of the $\beta$-rays (photo-electrons), $h\nu$ the incident photon energy and $E_B$ the electron binding energy.

The technique, however, soon lost favour to the newer techniques of X-ray absorption and X-ray emission spectroscopy.

XPS did not re-emerge until the early 1950s when Siegbahn and co-workers studied the photoelectrons with high resolution energy spectrometers (141). In 1954 the first X-ray photo-electron spectrum from cleaved sodium chloride was obtained. They were also the first to observe the chemical shift effect on core-level binding energies and continued the work to develop the whole field of electron spectroscopy during the period 1955-1970.

Since the late 1960's, ESCA (electron spectroscopy for chemical analysis) equipment has been available from several different companies. The addition of an ion source for sputter removal of surface layers made it possible to construct chemical depth profiles. Data is now usually handled by computer in a digital form, enabling more sophisticated interpretation of the qualitative and quantitative attributes of an ESCA spectrum. ESCA equipment is now used throughout the world in areas such as microelectronics, metallurgy, catalysis, polymer technology and corrosion science.
3.1.2 XPS Theory

3.1.2.1 The Photoemission Process

Any electromagnetic radiation with energy greater than the work function may excite secondary emissions of both photons and electrons from a material. In order to acquire information about the electron energy levels in the specimen it is necessary to use a radiation source of well defined energy.

Photon sources can be grouped into three categories. Those falling into the first category are differentially pumped inert gas discharge lamps which produce discrete low energy resonance lines (e.g. HeI 21.2ev and HeII 40.8ev) with an inherent width of a few meV. Since they possess only sufficient energy to emit electrons from the valence band, they are widely used in the study of the valence orbitals of molecules, electron band structure of metals, alloys and semiconductors and of adsorption phenomena (142). These sources provide an ultra-violet source, hence are used in the technique referred to as ultra-violet photoelectron spectroscopy (UPS).

The second category includes the characteristic X-rays which have higher energies and broader line widths. The two most used are Al Kα and Mg Kα X-radiations. Due to the higher energy they possess, they can excite electron from core orbitals. Where variable energy source are occasionally needed, other characteristic X-rays, such as Si Kα, Zr Lα and Ag Kα radiations have been used.

Possible excitation sources for XPS together with their energies and linewidths are listed in the following table.
Table 3.1

<table>
<thead>
<tr>
<th>Source</th>
<th>Energy, eV</th>
<th>Linewidth, meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>He I</td>
<td>21.22</td>
<td>3</td>
</tr>
<tr>
<td>He II</td>
<td>40.82</td>
<td>17</td>
</tr>
<tr>
<td>Mg Kα</td>
<td>1253.6</td>
<td>680</td>
</tr>
<tr>
<td>Al Kα</td>
<td>1486.6</td>
<td>830</td>
</tr>
<tr>
<td>Si Kα</td>
<td>1739.4</td>
<td>1000</td>
</tr>
<tr>
<td>Zr La</td>
<td>2042.4</td>
<td>1600</td>
</tr>
<tr>
<td>Au Mα</td>
<td>2122.9</td>
<td>2150</td>
</tr>
<tr>
<td>Mo Lα</td>
<td>2293.2</td>
<td>1900</td>
</tr>
<tr>
<td>Ag Lα</td>
<td>2984.3</td>
<td>2600 (1300)</td>
</tr>
<tr>
<td>Ti Kα</td>
<td>4510.9</td>
<td>2000</td>
</tr>
<tr>
<td>Cr Kα</td>
<td>5417</td>
<td>2100</td>
</tr>
<tr>
<td>Cu Kα</td>
<td>8055</td>
<td>2500</td>
</tr>
</tbody>
</table>

A third source of photons for photo-electron spectroscopy is synchrotron radiation — the radiation emitted by accelerating electrons. Electrons circulated continuously in a storage ring at energies of ~1 GeV produce a continuous spectrum of photons with
energies from a few eV to several keV. With a monochromator, therefore, a variable energy photon source is provided and this has several attractions for photoelectron spectroscopy (143-144).

Fig 3.1 shows the process of photoelectron and Auger electron emission diagrammatically. When a sample is irradiated with monochromatic photons of frequency $v_x$ electrons from the orbitals of the atoms with binding energy $E_b$ are excited, and released with a kinetic energy $E_{KR}$.

The Einstein relation governing the interaction of a photon with a core level is:

$$E_{KR} = h v_x - E_b - \Phi$$  \hspace{2cm} (3-2)

where $E_{KR}$ = kinetic energy of ejected photo-electron

$h v_x$ = characteristic energy of incident X-ray photon

$E_b$ = binding energy of core level electron

(with respect to the Fermi level)

$\Phi$ = spectrometer work function

Thus the electrons emitted have a specific kinetic energy characterizing the elements present in the sample surface.

The binding energy may be regarded as an ionization energy of the atom for the particular shell involved. Since there is a variety of possible ions from each type of atom, there is a corresponding variety of kinetic energies of the emitted electrons. Moreover, there is a different probability, or cross-section for each process. The variety of ionization processes for iron and uranium is shown schematically in Fig 3.2 (145). The Fermi level corresponds to zero binding energy (by definition) and the depth beneath the Fermi level in the figure indicates the relative energy of the ion remaining after electron
Fig. 3.1 Energy level diagram illustrating the Auger and photoelectron process

Fig. 3.2 Relative ionization cross-sections and ionization energies for iron and uranium (145)
emission, or the binding energy of the electron. The lengths of the lines indicate the relative probabilities of the various ionization processes. It is clear that the core levels have variable intensities, and that non-s level are doublets. The spectroscopic nomenclature is shown in the Table 3.2 (146) which is directly equivalent the X-ray and is more obviously related to the various quantum numbers.

Table 3.2 X-ray and spectroscopic notation

(After D. Briggs)

<table>
<thead>
<tr>
<th>Quantum numbers</th>
<th>X-ray suffix</th>
<th>X-ray level</th>
<th>Spectroscopic level</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>l</td>
<td>j</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1/2</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>3/2</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
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<td>1/2</td>
<td>2</td>
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<tr>
<td>3</td>
<td>1</td>
<td>3/2</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>3/2</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>5/2</td>
<td>5</td>
</tr>
<tr>
<td>etc.</td>
<td>etc.</td>
<td>etc.</td>
<td>etc.</td>
</tr>
</tbody>
</table>
The relative intensities of the doublet peaks are given by the ratio of their respective degeneracies \((2j+1)\). Thus the area ratio and designations of spin-orbit doublet are given in Table 3.3 (146).

<table>
<thead>
<tr>
<th>Subshell</th>
<th>j values</th>
<th>Area ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>1/2</td>
<td>–</td>
</tr>
<tr>
<td>p</td>
<td>1/2, 3/2</td>
<td>1:2</td>
</tr>
<tr>
<td>d</td>
<td>3/2, 5/2</td>
<td>2:3</td>
</tr>
<tr>
<td>f</td>
<td>5/2, 7/2</td>
<td>3:4</td>
</tr>
</tbody>
</table>

Equation (3.2) holds only when a conducting specimen is in good electrical contact with the specimen holder and thus with the spectrometer. Poor conductivity produces an electrostatic charge on the specimen, which results in the uncertainties in the peak position. Sample charging causes a shift in the energy scale, and in order to determine accurate absolute binding energies some form of referencing back to the Fermi level is required. The core level electrons from noble metals, e.g., those of Au 4f<sub>7/2</sub> and Ag 3d<sub>5/2</sub> have been commonly used for the absolute calibration of the spectrometer. These standards are then used to calibrate the secondary standard.

The carbon 1s electron binding energy from adventitious carbon found on most specimens is widely used as the secondary energy reference in
electron spectroscopy. The origin of carbon contamination is thought to be, in the part, from diffusion pump oil diffusing back into the spectrometer. The binding energy of C 1s level must be determined for a specific system but has commonly been found to be 284.8 (147).

Fig 3.1 also shows other processes normally accompanying the photoelectron emission by X-ray excitation.

One of them is the emission of the Auger electrons, named after its discoverer Pierre Auger. This process will be discussed in detail in Section 3.2.2. These Auger electron peaks excited by X-ray can also be used to identify the element. Beside that, the kinetic energy of Auger electron is independent of the excitation X-ray energy used to excite the initial core-hole state. This fact may be used to select the appropriate X-ray source to overcome the problem of overlapping between the photo- and Auger-electron peaks in the XPS spectrum.

Another process accompanying the X-ray photoelectron is the X-ray fluorescence (XRF) process. The vacancies left in the inner shells following photoelectron emission are filled by electrons from the outer shells and the transitions are accompanied by emission of radiation corresponding to the energy difference between the two shells. The measurement of the characteristic energies of the emitted X-ray forms the basis for X-ray fluorescence spectroscopy (XRF).

3.1.2.2 Chemical State Information

An important advantage of XPS is the ability to obtain information on the chemical state. There are three methods used normally for the identification of the chemical state:
3.1.2.2 A Chemical Shifts and Auger Parameter

The systematic shift in photoelectron and Auger line positions resulting from changes in the chemical structure and oxidation state of chemical compounds has been under investigation since Siegbahn et al (148) discovered that the chemical difference between copper and its oxide was clearly distinguishable by XPS.

The loss in electron density around a cation sets off an increase in binding energy of a few electron volt from the position found for its parent element. Anions show a corresponding decrease in the binding energy. It is this increase or decrease in binding energy — the chemical shift — that provides the information about the valence state of elements. While many attempts have been made to calculate chemical shift and absolute binding energies, the factors involved, especially in the solid state, are imperfectly understood and one must rely on experimental data on standard materials.

Since occasional line interferences do occur, it is sometimes necessary to use a line other than the most intense one in the spectrum. Chemical shifts are very uniform among the photoelectron lines of an element, so that line separations rarely vary by more than 0.2 eV. Exceptional separations, however, can occur in paramagnetic materials because of multiplet splitting.
Chemical shifts occur with Auger lines as well with photoelectron lines. The chemical shifts of Auger peaks are different from those of the photoelectron lines, however, and are considerably more pronounced in certain parts of the periodic table (149). Changes in chemical state are reflected in the fine structure which may be as pronounced as an actual shift in the peak position. Whether or not the chemical state can be recognised in this way depends on the width of the Auger peak. For the Auger processes in which the final vacancies arise in core levels it is clear that a change in chemical state giving rise to a chemical shift in the photo-electron lines will also produce a chemical shift in the Auger lines. The magnitude of the Auger chemical shift is often significantly greater than that of the photo-electron chemical shift, e.g., the KLL Auger peaks of Mg, Si, Al. Unfortunately, however, in many Auger processes the initial core hole is filled by electrons arising from the band structure of the solid and the degeneracy of these creates very wide peaks in which it is difficult to see chemical state information.

The Auger shift can be very useful for identification of chemical states especially in combination with photoelectron chemical shift data. The difference in binding energy between the photoelectron and Auger line is called as Auger parameter $\alpha$ (150, 151).

$$\alpha = E_{br}^p - E_{br}^a = E_{kr}^a - E_{kr}^r$$  \hspace{1cm} (3-3)

where $E_{br}^p$ = the binding energy of photoelectron  
$E_{br}^a$ = the binding energy of Auger electron  
$E_{kr}^a$ = the kinetic energy of Auger electron  
$E_{kr}^r$ = the kinetic energy of photoelectron

This difference can be accurately determined because static charge
corrections cancel. Then with all kinetic energies and binding energies referenced to the Fermi level,

\[ E_{k}^{p} = hv - E_{b}^{p} \quad (3-4) \]

\[ E_{k}^{a} + E_{b}^{p} = hv + \alpha \quad (3-5) \]

or, the sum of the kinetic energy of the Auger line and the binding energy of the photoelectron equals the Auger parameter plus the photon energy. A plot showing Auger kinetic energy versus photoelectron binding energy then becomes independent of the energy of the photon.

3.1.2.2.B Satellite Peaks

Several types of satellite are observed in photoelectron spectra. The following describes their various spectral features.

(1) X-ray satellites

The X-ray emission spectrum used for irradiation exhibits not only the characteristic X-ray, but some minor X-ray components at higher photon energies. For each photoelectron peak that results from the Ka X-ray photons, there is a family of minor peaks at lower binding energies, with intensity and spacing characteristic of the X-ray anode material. The pattern of such satellites for Mg and Al is shown in Table 3.4.

The X-ray satellites have no value in chemical analysis. When fitting the peaks of some transition metals such Cr 2p and Fe 2p, however, the Ka \(3\) satellite of the 2p\(1s2\) state has to be subtracted from the 2p\(3s2\) peak. A more detail description has been given by Richardson and Abu-Talib (152, 153).
Table 3.4

<table>
<thead>
<tr>
<th></th>
<th>$\alpha_1 %, \alpha_0 %$, $\alpha_4$, $\alpha_6$, $\alpha_8$, $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg displacement. ev</td>
<td>0, 8.4, 10.2, 17.5, 20.0, 48.5</td>
</tr>
<tr>
<td>relative height</td>
<td>100, 8.0, 4.1, 0.55, 0.45, 0.5</td>
</tr>
<tr>
<td>Al displacement. ev</td>
<td>0, 9.8, 11.8, 20.1, 23.4, 69.7</td>
</tr>
<tr>
<td>relative height</td>
<td>100, 6.4, 3.2, 0.4, 0.3, 0.55</td>
</tr>
</tbody>
</table>

(2) Shake-up lines

Not all photoelectric processes are simple ones, leading to the formation of ion in the ground state. Rather often, there is a finite probability that the ion will be left in an excited state, a few electron volts above the ground state. In this event, the kinetic energy of the emitted photoelectron is reduced, with the difference corresponding to the energy difference between the ground state and the excited state. This results in the formation of a satellite peak a few electron volts lower in kinetic energy (higher in binding energy) than the main peak. In some case, most often with paramagnetic compounds, the intensity of the shake-up satellite may approach that of the main line. More than one satellite of a principal photoelectron line can also be observed. Fig 3.3 shows an example of shake-up lines observed with the copper 2p spectrum. Such satellites are observed as a characteristic feature of Cu(II) 2p spectrum but not found in Cu(I).
Fig. 3.3 Examples of shake-up lines observed with the copper 2p spectrum (145)

Fig. 3.4 Some effects of chemical state on Auger line shapes (44)
compounds or in the metal (154, 155).

The satellite lines are caused by charge transfer transitions from the ligands (O\textsuperscript{2-} ions for the oxides) into the empty d-states of the central ion. Thus in the case of CuO, with a d\textsuperscript{9} configuration, there is one empty d-state which can get populated by a charge transfer transitions from a neighbouring oxygen ligand; in Cu\textsubscript{2}O, with a d\textsuperscript{10} ground state configuration such a transition cannot occur, which explains the absence of the strong satellites in this material. Hufner (156) suggested that there is always a finite probability that two electrons are ejected by one photon.

Satellites may also occur in the spectra of metals, they are, however, less common and also the mechanism is slightly different. Kotani and Toyozawa (157) have worked out the theory of satellites in metals in detail and give the following conceptually simple interpretation. Upon photoionization, the effective charge acting on the valence electrons is increased by one. Thus empty d-states that were before photoionization above the Fermi energy are now pulled down below it. These d-states can be either full or empty, the empty case corresponding to the satellite described above. So the view now held is that satellites occur if the photoionization is accompanied by a transition which promotes an electron from a filled valence band state into an empty conduction band state (156). The displacements and relative intensities of shake-up satellites can sometimes be useful in identifying the chemical state of an element.

The occurrence of such lines is sometimes more apparent in Auger spectral contours, of which an example is presented in Fig 3.4 (44).

With transition elements and rare earths the absence of shake-up
satellites is usually characteristic of the elemental or diamagnetic states. Prominent shake-up patterns typically occur with paramagnetic states.

(3) Multiplet Splitting

Multiplet splitting of core-level peaks can occur when the system has unpaired electrons in the valence levels. As an example, consider the case of the 3s electron in the Mn$^{2+}$ ion. In the ground state the five 3d electrons are all unpaired and with parallel spins. After ejection of the 3s electron a further unpaired electron is present. If the spin of this electron is parallel to that of the 3d electrons then exchange interaction can occur, resulting in a lower energy than for the case of anti-parallel spin. Thus the core level will be a doublet and the separation of the peaks is the exchange interaction energy (146).

Splitting also occurs in the ionization of p level, but the result is more complex and subtle. In favourable cases, it results in an apparent slight increase in the spin doublet separation, evidenced in the separation of the 2p$_{1/2}$ and 2p$_{3/2}$ lines in first row transition metal, and the generation of a less easily noticed asymmetry in the line shape of the components. Often such effects on the p doublet are obscured by shake-up lines (158).

Sometimes, the multiplet splitting phenomenon can be helpful in identifying chemical states. For example, such satellites appear in the 2p spectrum of Ni(II) and Co(II) ions but are not prominent in either the metallic or other valence states (153).
(4) Energy Loss Lines

With some materials, there is an enhanced probability for loss of a specific amount of energy due to interaction between the photoelectron and other electrons in the surface region of the sample. With metals, this effect is often more dramatic than that of insulators. Energy loss to the conduction electrons occurs in well-defined quanta characteristic of each metal. The photoelectron line, or the Auger line, is successively mirrored at intervals of higher binding energy, with reduced intensity. The energy interval between the primary peak and the loss peaks is called the plasmon energy. The so-called "bulk plasmons" are the more prominent of these lines. A second series, the "surface plasmons", exists at energy intervals determined by dividing the bulk plasmon energy by $\sqrt{2}$. The effect is not easily observable in non-conductors, nor is it prominent in all conductors (145). Plasmon lines have little analytical value. Under certain conditions they can cause confusion.

3.1.2.3 Sensitivity Factors

To quantify the XPS spectrum the area from the main peak of each element is obtained from the spectrum. These peak areas are then divided by appropriate sensitivity factors in order to obtain the relative proportions of each element present as an atomic %. The sensitivity factors used are applicable only to a given instrument type and excitation source and experimentally determined by running standards.

The intensity of an element, $I_A$, is presented relative to the F is
intensity, which has been used as a standard. The sensitivity factor, $S_A$ of the element A is given by

$$S_A = \frac{I_A}{n_A} / \frac{I_F}{n_F}$$

(3-6)

where $I_A = \text{intensity of element A}$

$I_F = \text{intensity of the reference element fluorine}$

$n_A = \text{stoichiometry of element A}$

$n_F = \text{stoichiometry of element F}$

Methods for quantifying the XPS measurement utilizing peak area sensitivity factors and peak height sensitivity factors have been developed. The former is more accurate because it is difficult to take account of the effects of peak shift and broadening due to different valence states when using peak height. In addition, intensity is also lost from the peak by shake-up events. The use of peak area may remove many of the problems associated with peak height measurements and has been adopted by many workers (159-165).

The sensitivity factors used throughout this work are those based on peak areas which are obtained from the analysis of the standards in this research group some years ago (166, 167). These values are listed in Table 3.5. They are similar to the determinations made by Jogensen and Berthou (159, 160).
### Table 3.5 Sensitivity factors

<table>
<thead>
<tr>
<th>Element</th>
<th>Is</th>
<th>Cr 2p₃/₂</th>
<th>Mn 2p</th>
<th>Fe 2p₃/₂</th>
<th>Ni 2p₃/₂</th>
<th>Mo 3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>0.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>2.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.73</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ar</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### 3.1.3 XPS Spectra

Fig 3.5 (146) depicts a wide scan spectrum of a clean silver surface obtained using Mg Kα radiation and an analyser operating in the constant pass energy mode (constant dE). A series of peaks are observed on a background which generally increases to low kinetic energy (high binding energy) but which also shows step-like increases on the low kinetic energy side of each significant peak.

When the X-ray source is non-monochromatic, the X-ray spectrum consists of a broad continuous distribution (Bremsstrahlung radiation) upon which are superimposed lines characteristic of the target (anode) material.

Equation (3.2) \( E_{\text{KX}} = h\nu_{\text{K}} - E_{\text{B}} - \Phi \) assumes that the photo-emission process is elastic. Thus each characteristic X-ray will give rise to a series of photo-electron peaks which reflect the discrete binding energies of the electrons present in the solid. The photo-emission
Fig. 3.5 X-ray photo-electron spectrum of silver excited by Mg Kα (essentially Mg Kα₁,₂) and recorded with a constant analyser energy of 100 eV (*Ag 3d 'satellite' excited by Mg Kα₃,₄) (after Briggs and Riviere, (146))
process is inelastic if the photo-electron suffers an energy change between photo-emission from an atom in the solid and detection in the spectrometer. The background 'step' to low kinetic energy of the photo-electron peaks is due to inelastic photo-emission (energy loss within the solid). Photo-emission by Bremsstrahlung radiation gives rise to a general background which is dominant in the low binding energy region of the spectrum. Secondary electrons result from inelastic photo-emission and increasingly dominate the background at lower kinetic energy.

The peaks observed in Fig 3.5 can be grouped into three basic types: peaks due to photo-emission from core levels and from valence levels and peaks due to X-ray excited Auger emission.

3.1.4 XPS Instrumentation and Data System

The basic components of an X-ray photoelectron spectrometer consist of an X-ray source for excitation, an electron energy analyser, some form of detection and control system as well as a high vacuum pumping system.

The standard X-ray gun consists of a heated-filament cathode from which electrons are accelerated toward a target anode over a potential of the order of 5-20 kV. Electron bombardment of the target anode causes the emission of X-rays, Bremsstrahlung radiation and electron. A thin, X-ray transmitting window (usually aluminium) separates the excitation region from the specimen and acts as a filter to reduce the Bremsstrahlung intensity. The choice of an anode material and operating
Fig. 3.6  X-ray source

Top, air view of filament and water connections
conditions is made to achieve the closest possible approximation to a single, intense, monochromatic X-ray line.

The anode materials utilized in the equipment used for the XPS analyses in this work are Mg and Al, so that either Mg Kα or Al Kα X-rays can be generated. Maximum power is 480 W for Mg Kα and 1 kW for Al Kα. A power of approximately 260 W (13kV, 20mA) was usually employed. Fig 3.6 shows a section through the X-ray source.

The electron energy analyser which measures energies of electrons emitted or scattered from a surface is the heart of the instrument. Electrostatic analysers are used in all commercial spectrometers. A variety of analyser geometries has been adopted in electron spectroscopy. The two principal ones are the concentric hemispherical analyser (CHA) and the cylindrical mirror analyser (CMA), which are both dispersive analysers, that is to say, in each the action of a deflecting electro-static field disperses the electron energies so that for any given field only those energies in a certain narrow range are measured.

Fig 3.7 shows schematic plan of a hemispherical photoelectron analyser. Before reaching the spectrometer, the photoelectrons are slowed by a retarding field, then pass through variable entrance slits. Electrons of the correct energy then pass through the analyser, and exit via a variable exit slit where the channeltron is mounted. The retarding field voltage is controlled by a ramp generator which may be driven by the instrument controls or by the data system.

The hemispherical analyser acts as a narrow pass filter letting through only electrons with an energy $E = HV$, where $V$ is the potential
Fig. 3.7 Diagram of photoelectron analyser
difference between inner and outer hemispheres and $H$ is a constant
determined by the physical dimensions.

The photoelectrons from the sample are retarded to an energy of $HV$
by the potential difference applied between the specimen earthed and the
electrical centre point of the hemispheres.

If $K$ = kinetic energy of photoelectron

$$R = \text{retarding voltage}$$

then $K = R + HV + W$ \hspace{1cm} (3-7-1)

or $K = R + E + W$ \hspace{1cm} (3-7-2)

where $W$ is a constant, the work function of the spectrometer.

In practice the analyser lets through electrons having an energy
range $E + dE$, where $dE$ would be the full width at half height of a
recorded peak assuming negligible source and specimen line widths, e.g.
the absolute resolution.

The relative resolution $dE/E$ of the hemispherical analyser is given
by

$$dE/E = \frac{\Delta r}{r + \alpha^2}$$ \hspace{1cm} (3-8-1)

where $r$ = mean radius of hemisphere

$\Delta r$ = slit width

$\alpha$ = half angle of admission of electrons

$E$ = pass energy

For a given geometry $dE/E$ is constant, $dE$ increases linearly with $E$.

The actual spectral resolution in XPS is also governed by the
natural X-ray line width. The K$\alpha$ lines used are actually doublets
containing the K$\alpha_1$ and the K$\alpha_2$. The natural line width of each
component is about 0.5 eV, but the doublet width is effectively 1.0 eV
for aluminium and 0.7 eV for magnesium. The peak width, defined as the full width at half-maximum (FWHM). \( \Delta E \) is a convolution of several contributions:

\[
\Delta E = (\Delta E_N^2 + \Delta E_P^2 + \Delta E_A^2)^{1/2}
\]

where \( \Delta E_N \) = the natural or inherent width of the core level

\( \Delta E_P \) = the width of the photon source (X-ray line)

\( \Delta E_A \) = the analyser resolution

[\( \Delta E_A \) is equal to \( dE \) in (3-8)]

The detectors currently used in X-ray photoelectron spectroscopy are based on continuous-dynode electron multipliers of the channeltron type (168, 169). These consist of curved glass tubes, which have the inner surface coated with a high-resistance semiconducting material possessing a high secondary-electron emissive power (168). A high voltage of a few kV is applied between the ends of such a tube, and multiplications of \( 10^6-10^8 \) are achieved by repeated wall collisions as electrons travel down the inside of the tube. The final output of detector, which is a series of pulses, is fed into a pulse amplifier/discriminator and interpreted via a data handling system i.e. multichannel analyser and computer.

The instrument used in this investigation is an ESCA-3 MkII photoelectron spectrometer of VG Scientific Limited, U.K. Fig 3.8 is a schematic diagram.

The resolution of the peak is given by the following equation:

\[
dE = \Delta r \ast E / 2R
\]

where \( R \) = Mean radius of the hemispherical sector (10 cm).
Fig 3.8 Schematic diagram of ESCA 3 MARK II
The 150° spherical sector analyser can be operated with a fixed pass energy of 2, 5, 10, 20, 50 and 100 eV according to the resolution required. For this work, when a pass energy of 50 eV and a slit width of 0.4 cm is used, the nominal resolution is 1.0 eV.

The data system used controlling the ESCA-3 is a VG 3040 comprising a Digital Equipment Corporation (DEC) PDP8e computer with 12k words of memory. The layout of PDP8e system is shown diagrammatically in Fig 3.9. It is not only interfaced to the spectrometer but also to an X-Y plotter, a VDU, a teletype for controlling the equipment and to disc drives.

Before data acquisition is started, a few parameters have to be input by the user, such as the time spent at each channel, channel width, the times of scanning and so on. Many different regions of the photoelectron spectrum can be scanned. The number of counts from the channeltron are summed then the voltage is stepped to the next channel. The acquisition is stopped after the scanning period has been reached. The wide scan is useful for identifying which elements are present but this is usually followed by analysing specific regions of photoelectron spectrum using a smaller energy window of 20-40 eV around the peak of interest. These narrow scans are used to obtain information about the chemical state of the particular element, and to provide accurate peak areas from which the element percentage can be calculated.

The acquired data are stored in discs, and can subsequently be manipulated at a visual display unit (VDU) attached to the system.

In order to quantify the elements present in an XPS spectrum it is necessary to obtain the peak areas for one of the main peaks from each
Fig. 3.9  Layout of the PDP8e and peripherals
element. This can be done by subtracting a linear background from the peak using VDU. The computer provides a routine whereby the user can place a straight line where he chooses on the spectrum displayed on the VDU. The area beneath the straight line is subtracted from the area of original peak. The area obtained after subtraction, together with the peak position, the maximum and minimum counts in the before-subtracted region, are printed at the teletype.

Data can also be transferred from PDP8e system to the University Prime computer which provides a variety of facilities for the acquired XPS data. The peak fitting routine has been used to synthesise the acquired spectrum into peaks with different widths, positions, shapes and backgrounds. Details of this routine and the quantification of chemical state information in transition metal peaks will be discussed in Chapter 4.

The other facilities provided on Prime are peak-labelling, smoothing and baseline subtraction. All these were established by Richardson (152) and documented in his Ph.D thesis.
3.2 Auger Electron Spectroscopy (AES)

3.2.1 Introduction

Pierre Auger first discovered in 1925 (170) that ionized atoms could approach the ground state by a radiationless transition, i.e., emission of Auger electrons rather than photons. Lander (171) in 1953 recognized that Auger electrons could be used for elemental analysis of surfaces, but the Auger intensities were too weak to be used routinely. In the late 1960s, Harris (172) showed that the Auger signal/background ratio could be enhanced by taking the derivative of the signal, thus recording the dN(E)/dE rather than the N(E) spectra. From this beginning, the use of AES has grown rapidly and today it is the most widely used surface analytical technique. Nowadays, Auger electron spectrometers are coupled with finely focused scanning electron microscopes and used in conjunction with inert gas ion sputtering for sample depth profiling.

3.2.2 Auger Process

As shown in Fig 3.1, an incident electron, photon, or even an ion may create a core hole by ejecting an ionizing electron. Ionized atoms approach the ground state by filling core holes with electrons from an upper level. The energy difference causes emission of a photon or an Auger electron, where the sum of the probability of emission of a photon or an Auger electron is unity. For energy differences below about 2000 eV, the probability of Auger emission is near unity. As a result, light elements (atomic number < 14) de-excite almost exclusively by Auger emission. Auger electrons are emitted by all elements with Z > 3.
Fig. 3.10 Schematic diagram of the process of Auger emission in a solid.
Auger emission is a de-excitation process which can be initiated in a number of different ways, e.g. X-rays, electrons, or ions. In Section 3.1.2.1, the Auger emission which is initiated with X-rays has been mentioned. By convention, AES refers to spectroscopy performed with electron excitation.

Fig. 3.10 is a schematic diagram of the process of Auger emission in a solid. The ground state of the system is shown at the left. In the centre an incident electron of energy $E_p$ has created a hole in the core level $K$ by ionization; for this to occur efficiently $E_p$ should be greater than $\sim 5E_K$. The hole in the $K$ shell is filled by an electron from $L_{2,3}$, releasing an amount of energy $(E_K - E_{L_{2,3}})$, which can appear as a photon of energy $h\nu = E_K - E_{L_{2,3}}$ or can be given up to another electron. In this example, the other electron is also in the $L_{2,3}$ shell, and it is then ejected with energy $(E_K - E_{L_{2,3}} - E_{L_{2,3}}^{*})$; $E_{L_{2,3}}^{*}$ is starred because it is the binding energy not of $L_{2,3}$ in its ground state, but in the presence of a hole in $L_{2,3}$. The doubly ionized final state is shown on the right.

The Auger transition depicted in Fig. 3.10 would be named in the conventionally used j-j coupling $KL_{2,3}L_{2,3}$. The energy of the ejected Auger electron here is

$$E_{KL_{2,3}L_{2,3}} = E_K - E_{L_{2,3}} - E_{L_{2,3}}^{*}$$  \hspace{1cm} (3-10-1)

The emitted Auger electron is escaping from the field of two holes. Considering the relaxation of the other electrons, a more accurate expression was obtained (173):

$$E_{KL_{1,2,3}} = E_K - \frac{1}{\hbar} \left( E_{L_1}(Z) + E_{L_1}(Z+1) \right) - \frac{1}{\hbar} \left( E_{L_{2,3}}(Z) + E_{L_{2,3}}(Z+1) \right)$$  \hspace{1cm} (3-10-2)
The \( Z+1 \) terms arise from the use of the equivalent cores approximation to represent the core-ionised element \( Z \) by the neutral atom \( Z+1 \).

It is clear that the Auger energy is a function only of atomic energy levels, so that for each element in the periodic table there is a unique set of Auger energies. Thus analysis of Auger energies immediately leads to elemental identification.

3.2.3 Characteristics of Auger Electron Spectroscopy

Because there are normally a number of Auger transition with characteristic energies, shapes, and patterns, the elemental resolution is good. Detection limits are typically 0.1% atomic (174).

Electron beams are normally used for AES, so spatial resolution in the plane of the surface can be very good. AES instrumentation is available with minimum electron beam sizes of 50 nm. The sensitivity at this resolution is substantially degraded since the signal intensity is a function of current striking the sample (174, 175). In order to achieve high spatial resolution the electron optics must be operated in a fashion that restricts the beam current to the sample.

The Auger electrons used for analytical purposes are ejected from the atoms in the solid with kinetic energies between 25 and 3000 eV. Electrons with such energies can travel only a short distance within the solid before they lose energy by collisions. Typically a 1000 eV electron has an inelastic mean free path of 15 Å and 95% of the electrons which escape from the surface come from within a depth equal to three times this value. Thus by observing those kinetic energies which correspond to Auger electrons escaping, the effective sampling
depth is only ~50 Å (176). Depth resolution, normal to the surface, is better than in the surface plane.

A spectrum derived from Auger electrons has a large background consisting mainly of backscattered primary electrons and inelastically scattered Auger electrons. This background is primarily set by the physics of the process and an important ratio is S/B = signal/background, where 'signal' is the number of Auger electrons emitted (without energy loss) within a given energy band (usually corresponding to the base width of the Auger peak), and 'background' is the number of 'secondary' or scattered electrons from the specimen which fall within the same energy band. An analyser with a high S/B ratio is useful for chemical shift measurements because the low background permits direct recording of N(E) spectra and hence accurate location of energies at peak centres (176).

3.2.4 Basic Instrumentation

In conventional AES, an incident electron beam is used to produce ionization in core levels in order to initiate the Auger transition. The two types of electron source used in AES are thermionic and field emission, and of these the former is by far the more common. A conventional tungsten thermionic filament is used for the great majority of electron sources, because it is relatively easy to make and to replace, its emission properties are entirely reproducible and it can be used over a wide range of emission currents although it may have a lower brightness. By using LaB₆, an emitter of lower work function, higher brightness can be obtained for thermionic emission. With progressively
improving technology, the emphasis will be placed more and more on the higher brightness sources.

A modern AES system is combined with SEM in order to make the best use of the high spatial resolution of AES. The position of an analytical point on the sample surface can be precisely located by the help of the SEM image.

AES is performed in an ultra-high vacuum. An electron spectrometer vacuum system fulfils two basic functions. Firstly, it has to reduce the pressure to a sufficiently low value that the emitted electrons can pass from the sample through the analyser without making too many collisions with residual gas molecules. Secondly, it must enable the sample surface to be maintained free from contamination by the constituents of the residual vacuum for a time adequate for recording the necessary spectra. This in practice is achieved in a bakeable system capable of better than $10^{-10}$ Torr ultimate pressure.

The presence of the electromagnetic lens and scan coils in the spectrometer column, makes bakeout difficult. These difficulties, however, have been largely overcome in the last few years.

Except for the production of the primary excitation beam and some related facilities for SEM, most of the devices used in AES, such as the electron energy analyser, the detector of the channeltron type are similar to those in XPS.
3.3 Ion Beam Profile

Ion sputtering has been used as a potential method of producing a clean surface on a sample. It is also used very extensively indeed, in conjunction with surface analysis, as a method of obtaining compositional information as a function of depth below the surface.

When used with XPS, in which data acquisition is slow, the information is built up stepwise, i.e. by alternate cycles of bombardment and of analysis. When used with AES, however, which is a relatively fast technique, the bombardment and analysis can be carried out simultaneously and a more continuous compositional profile is obtained. For AES the spatial distribution of the ion beam is not too critical as the electron beam used to generate the Auger electrons may be placed in the centre of the etched area. For XPS, the beam should etch uniformly over the area of several square millimetres which the exciting X-ray beam covers.

Hofmann has summarised the principle advantages of depth profiling by AES and XPS combined with ion sputtering as follows (177):

(1) The information depth is of the order of 1 nm.

(2) The analysis is independent of the sputtering yield.

(3) The influence of the matrix on the elemental detection sensitivity is small.

(4) The analysed area is small compared to the sputtered area, thus minimizing crater edge effects (which is generally not fulfilled in XPS).

It has become evident, however, that ion beam profiling is a complex technique, one should be aware of the artefacts that can be introduced by it.
3.3.1 Effects of Ion Sputtering

The effects of ion sputtering take the form of chemical (178) and/or topographical (179) changes induced in the surface.

3.3.1.1 Chemical Changes

Chemical changes mean the alteration in the elemental composition and/or chemical state, of the major constituents that can occur at the surfaces of alloys and compounds during ion bombardment.

3.3.1.1 A Preferential Sputtering

Under ion sputtering atoms are removed from the surface with different efficiencies (180, 181).

The sputtering yields, which are defined as the total numbers of atoms sputtered per incident ion colliding with the solid surface, vary substantially across the Periodic Table, as shown in Fig 3.11 from Seah (182). In a material containing two or more elements, some elements are removed preferentially due to the higher sputtering yield. Surface analysis after ion bombardment would therefore reveal a depletion in that element compared to the bulk or stoichiometric composition. Depletion continues with further bombardment until an equilibrium situation is reached in which the relative atom populations of elements at the surface is balanced by the relative sputtering yields. This effect has been observed frequently in alloy systems in which there is a significant disparity in sputtering yields between the constituents.
Fig. 3.11 Predicted values of the sputtering yields of argon ions of energies 500 and 1000 eV across the Periodic Table. The yields of several elements with particularly high sputtering yields are not shown, for the sake of clarity, but may be found in the original paper by Seah (182)
If the sputtering yield of the components is independent of their bulk concentration $C_b$, the surface composition $C_s$ is inversely proportional to the respective sputtering yield $S$ (183):

$$\frac{C_{sA}}{C_{sB}} = \frac{S_B}{S_A} \frac{C_{BA}}{C_{DB}}$$  \hspace{1cm} (3-11)$$

where the subscripts A and B denote the two components. This means that the element with the lower sputtering yield is enriched in the surface. Carbon, for instance, has a sputtering yield of an order of magnitude lower than many metals so that a stoichiometric carbide is enriched in carbon on sputtering (162).

The ratio of sputtering yields of different elements obtained from an alloy differs from that obtained from individual elements. This effect has been observed by many works (184-187). Sigmund et al (188) suggested that this is due to the matrix effects, in which the lighter element of a pair in a binary is preferentially sputtered. Thus an 'A' atom surrounded by 'A' atoms behaves differently from an 'A' atom in a 'B' lattice when impacted by a high energy ions beam.

The individual sputtering rates of some oxide have been measured. McIntyre and Zetaruk (189) have determined the sputtering rates of Fe$_2$O$_3$, NiO and Cr$_2$O$_3$ which were 4.0, 4.0, and 1.5 nm/min respectively under their sputtering condition. They also found, however, that Fe/Cr ratio remained constant during sputtering of the intimate mixture of Cr$_2$O$_3$ and Fe$_2$O$_3$, which prepared by co-precipitation, i.e. the lower sputtering rate of Cr$_2$O$_3$ did not cause preferential removal of other oxides.

Reidel et al (187) studied the the sputtering of Fe-Cr and Fe-Ni alloys by using SIMS. In the Fe-Cr alloys, it was found that the presence of iron increase the sputtering rate of chromium whilst the reverse is true for
chromium. A similar study of Fe-Ni alloys, however, showed little variation in sputtering yield.

By using their result, Richardson (152) suggested that the use of argon ion bombardment to provide a clean surface for corrosion would not to modify the surface composition of 18/8 stainless steel greatly.

3.3.1.1 B Ion Beam Induced Reaction

The other chemical changes induced by the beam sputtering can be equally serious. They include reduction or decomposition of compounds and persistence of elements due to 'knock-on' and reaction with species from external sources. Although each is considered separately, they are all inter-related and can influence the results of XPS analysis:

1) Beam induced decomposition or reduction

During ion sputtering the more volatile elements such as oxygen in oxides, sulphur in sulphides, etc, are lost preferentially even though their elemental sputtering yield may be similar to, or even lower than, those of the other constituents. Such loss is inevitably accompanied by a reduction of a metal oxide.

Kim et al (190), who first observed oxide decomposition by using XPS, found an approximate relationship between the standard free energy of formation of the oxides $\Delta G^\circ$ and their reducibility by argon ion bombardment with 400 eV ions. It is found that all oxides with $\Delta G^\circ$ below 60 kcal/mole were reduced while all those with $\Delta G^\circ$ above 108 kcal/mole, except MoO$_3$ and Fe$_3$O$_4$, were stable under the ion bombardment. In their investigation compact bulk oxides were used.
Holm and Storp (191) etched with 5 keV argon ions and reported the partial reduction of MoO$_2$ to lower valency oxides, reduction of Bi$_2$O$_3$ to Bi, and reduction of SiO$_2$, these oxides having appeared stable in the Kim et al study. The silicon reduction was found to occur at a beam intensity of 10 µA/cm but not at 1 µA/cm. Their experiments were carried out on thin oxides grown on unoxidised substrates. Their explanation for the dependency on the primary ion current density is that different recovery times are needed for restoration of the original state. The $\Delta G^*$ relationship of Kim et al is thought of as a measure of the metal-oxygen affinity, above which the reoxidation processes takes place so rapidly that at a given ion current density, no reduction phenomena can be detected by XPS unless the oxygen is bound in some way.

With the aid of the $\Delta G^*$ relationship we can estimate which species may decompose, although it will depend on the ion beam energy and current.

The following has been reported for iron, chromium and nickel.

Fe$_3$O$_4$ has been observed by some workers to be reduced to lower oxides or Fe (189, 192-195), however, work in this laboratory has shown that even after extensive etching haematite remained unchanged (196). McIntyre et al (197) observed the reduction of magnetite (Fe$_3$O$_4$) to FeO.

Cr$_2$O$_3$ was observed to be fairly stable (189, 190).

Assuming the mechanism of Holm and Storp (191) to be valid then in a mixed oxide, there would be a competing for oxygen between different species. For instance, in a mixed Fe/Cr spinel, reduction of the iron species is more likely, while the chromium becomes more stable.

Kim et al (190) observed the reduction of NiO to Ni, but not reduction of Ni(OH)$_2$ to NiO or Ni. A partial reduction of Ni(OH)$_2$ to NiO, however, has been observed by some workers (191, 192), but the reduction of NiO to
Ni has not been observed by McIntyre et al (197) and Chuang et al (193).

The effects discussed above can obviously lead to misinterpretation of chemical state information in XPS spectra. Different experimental conditions probably explain the variation in results between different research groups. The results in the literature can be used to give a approximate idea of the relative stability of species, but test specimens must still be run since results can vary widely according to the ion bombardment conditions.

(2) Recoil and knock-on effects

Ion bombardment may also cause depth resolution loss when ions in the superficial layer are knocked or diffused into deeper layer. In this effect, which is known as knock-on process, some elements, particularly light ones, can be driven further into the material by direct impact from a primary ion or by indirect impact via an energy cascade. This effect is directly dependent on the energy of the primary ions (198). In this investigation, it has been shown that for low energy ions, atoms from one depth are pushed forward to greater depths in the order of 3 nm.

This is the basis of Holm and Storp's (191) explanation why they observed the reduction of thin oxides on substrates, whereas Kim et al did not observe reduction of bulk oxide. They speculated that the capture of oxygen atoms by the substrate — due to either diffusion or knock-on (recoil implantation) — reduced the chance of the molecule relaxing to its original state. They observed the formation of low valence or non-stoichiometric oxides as an interim stage in reduction. As a consequence a sharp interface is homogenized. The persistence of carbon in certain materials during prolonged bombardment is generally attributed to this
effect (199).

It has not proved possible so far to take account in any systematic way of the artefacts of reduction and of 'knock-on' when attempting quantification in their presence.

(3) Contamination of the feed gas and specimen

Contamination of the gas, especially with oxygen, leads to interface broadening when profiling through oxides on metals. It takes only a small amount of oxygen contamination to make it impossible to etch chromium to the metallic state.

With the contamination the etching rate is reduced (200, 182) which means the estimated film thickness becomes higher. This also decreases the depth resolution as etching proceeds.

Another source of contamination is the analyser vacuum, which may contain traces of water vapour, that could be picked up by the ion beam. Carbon is also found to deposit from the vacuum onto specimens under analysis. Under the action of the ion beam it could react with other species on the surface to form some compounds, such as chromium, to form a carbide (191).

3.3.1.2 Other Effects

In addition to the chemical effects cited above, some other problems associated with the ion bombardment should be briefly mentioned.

The roughness of a surface can be increased by ion bombardment in several ways (201). If the ions are directed at the sample surface from one direction only, i.e. from a single source, then in general any
asperities tend to be accentuated since sputtering efficiency is greater at higher incident angles. A more serious situation can arise if there are impurity inclusions in the material whose sputtering yield is much less than that of the surrounding matrix. In this case the inclusion 'shadows' the material behind it from the incident ions and a conical pillar forms of progressively increasing height (202).

The shadowing effect also arises from the different angles subtended at the sample by the ion gun and the analyser analytical system. A non-uniform flux of ions used in the sputtering can also induce non-uniform surface erosion.

Ion bombardment in conjunction with XPS is widely used, and is certainly an effective tool to obtain compositional profiles. It is also clear that the effects discussed above can lead to misinterpretation of XPS spectra, which should be treated with extreme caution.

3.3.2 Instrumentation and Etch Condition

To clean or etch a specimen an argon ion gun AG2 VG Scientific, U.K (Fig 3.12) is mounted on the analyser vessel. It is a cold cathode source ion gun with ion beam extraction, acceleration and focussing. Ion beam energy can be controlled from 0 to 10 keV, and also be focussed by setting up the focussing voltage on the lens from 0 to 10 kV. The beam current depends on the accelerating electrode potential (which extracts the ions from the source) and on the argon pressure in the discharge, the order of 100 μA can be obtained. A very high purity of argon gas (99.999%) is used to avoid any unwanted chemical reactions occurring on the sputtered sample. A small trace of oxygen which is normally found in the argon gas is removed.
Fig. 3.12 The AG2 ion gun

Fig. 3.13 Principles of sputtering profile evaluation: conversion of a measured sputtering profile \( I = f(t) \) to a true concentration profile \( c = f(z) \) (after Hofmann, (203))
by passing the argon though a small in-line furnace containing titanium granules, before bleeding into the analyser chamber.

General experience in the laboratory, has suggested the following etch conditions:

<table>
<thead>
<tr>
<th></th>
<th>ESCA3MkII</th>
<th>MA500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam energy, keV</td>
<td>3.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Focussing voltage, kV</td>
<td>1.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Beam current, µA</td>
<td>5-10</td>
<td>20-30</td>
</tr>
<tr>
<td>Argon pressure, Torr</td>
<td>$10^{-6}$</td>
<td>$5\times10^{-6}$</td>
</tr>
</tbody>
</table>

3.3.3 Depth Profile

The data primarily obtained during the depth profiling experiment consist of signal intensities of detected elements I as a function of sputtering time t, i.e. the measured 'sputtering profile' $I=f(t)$. The principal task is to obtain the original distribution of concentration $C$ with depth $z$, $C=f(z)$ by an appropriate conversion of the measured data. The principles of sputtering profile evaluation was shown as Fig 3.13 by Hofmann (203).

Ion etching was carried out for a fixed time intervals and the sputtered surface was analysed subsequently. In the case of XPS, the peak area for each element was determined by using straight line background. Then the peak area data were corrected using the sensitivity factors, (see Table 3.5, Section 3.1.2.3).

The atomic percentages for each element were calculated according to the relationship:
\[
\text{Atomic\% of element } a = \frac{N_a}{S_a} = \frac{\sum N_i/S_i}{i}
\]

where \( N_i \) = the peak area of element \( i \)
\( S_i \) = the sensitivity factor of element

Two forms of representing the depth profile were used in this work:

(1) Non-cumulative profile

In this representation, the Y-axis of the plot represents the actual atomic percentage of an element at a given etch time;

(2) Cumulative profile

The proportion of any species on the surface at time \( t \), is given by the distance between adjacent line on the graph.
3.4 XPS Angular Profile

As described in Section 3.3, the usual way of obtaining a compositional depth profile in electron spectroscopy is by in-situ erosion of the sample surface by a beam of inert gas ions, carried out sequentially with the analysis until the required depth is reached. It is, however, a destructive method.

By varying the electron emission angle (take-off angle), a non-destructive method of depth profiling can be achieved in XPS. It would be invaluable in determining the concentration gradients that exist within those oxide overlayers on the sample surface.

3.4.1 Basic Theory of Angular XPS

The basis of angular XPS is the increase in surface sensitivity obtained at low angles of electron exit to the surface. Fig 3.14 shows surface sensitivity enhancement by variation of the electron 'take-off' angle (146).

If $\lambda$ is the inelastic mean free path (IMFP) of the emerging electron then 95% of the signal intensity is derived from a distance $3\lambda$ within the solid. The vertical depth sampled is given by

$$d = 3\lambda \sin \theta$$  \hspace{1cm} (3-13)

and this is a maximum when $\theta = 90^\circ$. In the case of substrate (S) with a uniform thin overlayer (O) the angular variation of intensities is given by

$$I_{S}^{\theta} = I_{S} e^{-d/\lambda \sin \theta}$$  \hspace{1cm} (3-14)

and $$I_{O}^{\theta} = I_{O} (1 - e^{-d/\lambda \sin \theta})$$  \hspace{1cm} (3-15)

where $\lambda$ is the appropriate value for the observed photo-electron. In the
Fig. 3.14 Surface sensitivity enhancement by variation of the electron 'take off' angle (After Briggs and Rivière (146))

\[ d = 3 \lambda \sin \theta \]

Fig. 3.15 Theoretical angular dependent curves for a clean flat surface and a flat overlayer/substrate system (After Briggs and Rivière (146))
ideal situation these equations lead to curves of the type shown in Fig 3.15 (146).

As an example, Fig 3.16 (1), wide-scan spectra are shown at various angles for a highly-polished silicon specimen with an oxide overlayer 1-2 atomic layers in thickness, and an outermost overlayer of carbon-containing residual gas impurities of approximately the same thickness (204). Pronounced peaks due to the O 1s, C 1s, Si 2s and Si 2p core levels are observed. At the higher emission angles of 40° and 70°, plasmon loss structure is found to be associated with the Si peaks. As θ is lowered to a grazing exit condition, marked changes occur in the relative intensities of all peaks. At high θ where maximum bulk sensitivity is expected, the intensity order is Si 2s, 2p > O 1s > C 1s, where at low θ with maximum surface sensitivity, it is C 1s > O 1s > Si 2s, 2p. If the Si 2p region for this specimen is examined more closely, it is further found to exhibit a chemical shift between oxide and element, as shown in Fig 3.16 (2).

The major requirement for surface sensitivity enhancement is that the surface is flat. The use of this technique is not valid for rough surface owing to

(1) an averaging of electron exit angles
(2) shadowing effects (both of the incident X-rays and emerging electrons).

3.4.2 Computer Modelling of the XPS Angular Profile

Castle (205) demonstrated how to calculate the thickness of thin uniform overlayers for oxide layers on metals using the equation (3-14).

When dealing with the oxide film growing on the surface of stainless steel
Fig. 3,16(1) Broad-scan spectra at low and high exit angles for a Si specimen with a thin oxide overlayer (~6 Å) and an outermost carbon contaminant overlayer approximately 1-2 monolayers in thickness. The C1s and O1s signals are markedly enhanced in relative intensity at low θ (after Fadley, 204)

Fig 3,16(2) Si2p core spectra at θ = 5° and 49° for the specimen of Fig. 3,16(1). The chemically-shifted Si2p (oxide) peak is enhanced in relative intensity by approximately a factor of 20 between 49° and 5° (after Fadley (204))
sample undergoing oxidation/reduction, however, the concentration of the elements in the film at different depths are not uniform but are variable according to whether elements are concentrated in the inner layer.

In this investigation, the computer routine on Prime, which was built by Watts and closely based on the formalism of Paynter (206), has been employed. Considering the analysis volume as a series of steps or slices, the electron emission from each slice can be calculated as can the electron attenuation as a result of the slices above it. This can be repeated in turn for each element in the analysis. Thus by postulating a depth profile it is possible to set up the various equations and undertake the calculations to predict the angular profile it generates.

This computer routine can be stated in a generalized form for a model profile with $j$ steps. Considering a single element as following:

$$I_0 = kF \lambda \sin \theta \left( n_1 + \sum_{N=1}^{j} \lambda \sin \theta \frac{n_{N+1}-n_N}{\lambda \sin \theta} \cdot \frac{-x_{2N-1} - x_{2N}}{\lambda \sin \theta} \cdot \frac{-x_{2N}}{\lambda \sin \theta} \right)$$

(3-16)

where $kF$ is an instrument constant and is eliminated in the calculations, $n_N$ is the atomic concentration at depth $x_N$, $\lambda$ is the electron inelastic mean free path.

Because of the large number of independent variables in the algorithm, the angular profile must be calculated from the postulated depth profile and compared with the experimental data. This procedure is then repeated on a 'trial-and-error' basis until there is good agreement between calculated and experimental data.

Referring to Watts (206), these are described in the flow diagram of Fig 3.17.
Fig. 3.17 Flow diagram of computer modelling of the XPS angular profile

- Record Survey Spectrum
- High Resolution Spectra C1S, O1S, Fe2p, Cr2p, Ar2p
- Change θ to 15°, 25°, 35°, 45°, 60°
- Five Angles
- Determine Peak Areas of High Resolution Spectra
- Calculate θ vs Atomic % Experimental Angular Profile
- Postulate Compositional Depth Profile
- Compute θ vs Atomic % for Postulated Composition Depth Profile
- Calculate Angular Profile
- Compare Calculated Angular Profile against Experimental Angular Profile
- Good Agreement
- Assume Profile Exists

Operator

University of Surrey PRIME 550 computer

V G Scientific ESCA 3 Mk. II & VG 3040 Datasystem
During the calculation of depth profile, 4 gram/cc is adopted as material density.

The values of electron inelastic mean free path are respectively:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>Fe</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$ Å</td>
<td>9.5</td>
<td>8.5</td>
<td>7.7</td>
<td>8.3</td>
</tr>
</tbody>
</table>

which were calculated within the computer routine using the formula of Seah et al (207).
3.5 The Energy Loss Feature of Photoelectron Peaks

X-ray photoelectron and Auger electron peaks of elements in a solid are always accompanied by the energy loss background. This background arises from those photoelectrons which have undergone inelastic collisions during their passage from the emitters to the surface of the solid. The photoelectrons thus lose energy and are shifted to a lower kinetic (high binding) energy side of the peaks giving a characteristic step in the background.

The background signal constitutes a major problem in the application of electron spectroscopy to surface analysis. Correction must be made for this effect before a determination of the true peak area or line shape is possible. On the other hand, however, the background signal and the distortions in electron spectra caused by inelastic scattering events during electron transport from the point of excitation to the surface depend on the depth distribution of electron emitters in the material. Therefore, the intensity and shape of the background signal will carry information on the depth distribution of a given element in the surface region of the material.

3.5.1 Post-peak Energy Loss Structure (post-peak slope or P-PS)

Tougaard et al (208-210) have investigated theoretically the influence of elastic and inelastic scattering on energy spectra of electrons emitted from solids for the case of a primary excitation function corresponding to a narrow line as in Auger and photoelectron spectroscopy. They
concentrated on the influence of elastic and inelastic electron scattering on the shape and intensity of the spectrum in the vicinity of the primary peak. It was shown that for XPS spectra from homogeneous samples a near-peak as well as an off-peak region can be identified. The critical total energy loss separating these two regions below a peak in the spectrum depends on the relative importance of elastic and inelastic scattering. In the off-peak region, where the electron typically has undergone several scattering events, the total energy loss is given by a continuous expression. It was suggested (211-213) that the variation in peak shape is characterised by a single parameter \( D = A_p/B \) which is the ratio of the XPS peak area to the increase in background signal 30 eV below the peak energy. For homogeneous metals \( D \) is to first order found to be a universal constant in good agreement with experimental results. For inhomogeneous metals, the ratio \( D = A_p/B \) was studied under variation of the path length \( R \) travelled by the photoelectron in the solid, the XPS peak energy \( E_p \), and the particular metal \( M \). It was found that \( D \) is first order independent of \( M \) and to a good approximation

\[
D (R, E_p) = \left( 425 + E_p \right) R^{-1.55} e^{1.4 \times 10^{-5} E_p} \tag{4-1}
\]

with \( E_p \) in eV, \( R \) in Å, and \( D (R, E_p) \) in eV. They suggested \( D \) could be used for fast non-destructive extraction of in-depth composition information.

They have also studied experimentally the background intensities in XPS spectra from homogeneous metals such as Cu, Ni, Ag, Pt, Ta, W, Mo (208-210, 213). They suggest that rather deeper structures can be probed by the use of background intensities than by the use of the peaks themselves.

Proctor et al (214) have studied inelastic background and peak area determination in XPS by analysis of the Au 4f spectra of thin gold films deposited over a graphite base. It was noted that there is a considerable
variety of background profiles, which can be encountered in real samples, and depends markedly on the element, its concentration, and its distribution in the sample.

Castle et al (215-216) have studied the behaviour of the energy loss spectrum over some range beyond the peak. A sample of pure chromium was etched by argon ions in the XPS spectrometer. Overlayers of titanium were then produced by successive evaporations. Fig 3.18 (215) shows the changes in the energy loss structure A-B of the chromium 2p peaks with increasing thickness of the titanium overlayer. There is a steady increase in the post-peak slope (P-PS) of chromium 2p with increase in overlayer thickness. Similar observations have been made on the spectrum of chromium with carbon contamination accumulated on the surface and with a heavy overlayer of aluminum.

It is notable that the peaks from the overlayers of titanium, which are responsible for the development of P-PS structure on the chromium, do not show any change in slope with increase in thickness. The energy loss structure is fully developed at a thickness of approximately twice the inelastic mean free path. The author suggested that this difference in background slope between overlayer and substrate is thus able to differentiate the relative position in depth of individual elements. Using the background slope as a function of peak height at a point about 50 eV lower in kinetic energy than the peak can reveal information relating to the layer sequences of surface elements. In a sense the P-PS can be a reliable indicator of order in practical situations.
Fig. 3.16 The changes in the energy loss structure A-B of the Chromium 2p peaks with increasing thickness of the titanium overlayer (after Castle, (215))
3.5.2 Energy Loss Tail Height (ELTH)

As mentioned above, in interpreting and analysing the photo-electron peaks, it is necessary to take into account the electrons which are inelastically scattered during its passage from the point of excitation to the surface of the metal. These electrons possess different energies from the elastically scattered ones and thus produce a low kinetic energy background (at higher binding energy region), overlapping with the main peak. This effect could be more pronounced for X-ray photoelectron peaks of transition metals which normally have two peaks very close to each other resulting from two different spin states of the same orbital angular momentum. For most groups of workers, this broad continuum of loss structure is removed by subtracting a Shirley background. Because of the advantage that the peak area is not sensitive to the start and end position of the subtraction, Shirley type background is widely used.

For those specimens which include two or more chemical states distributed in a layer-like fashion, as Castle et al (215-216) have pointed out, the energy loss background from the pure metal may overlap with the main peak of the oxidised metal due to the relatively wide energy range of the energy loss electrons emitted. Thus Shirley background which gives equal weight to both chemical states within the total peak envelope is inaccurate for a composite peak containing features from differing depths, because the distance travelled by electrons in the superficial phase is limited whereas that in the substrate is not.

A method of curve fitting which enables the energy loss feature of each peak component to be handled separately has been developed and modified
Considering that the contribution to the rise in background of each component would vary according to the depth distribution, this method of curve fitting allows each fitted component to be given an energy loss tail of constant height (ELTH). Just as the sum of the component peak is fitted to the peak envelope, the sum of the individual loss tail is fitted to the background rise. To separate the constant tail from the peak, each peak has its own 's' shaped background. When the peak contains two components such as those of an element and its ion, the value of ELTH of each component provides information on the depth distribution. For example, the background contribution from a surface oxide is less than that from the underlying metal. Hence an examination of relative energy loss intensities as indicated by the tail height will thus distinguish surface from bulk phase.

These energy loss structures provide a method to aid in characterisation of near surface distribution of elements and ions, and are particularly useful as a non-destructive technique when ion-etching is undesirable.
3.6 Energy Dispersive X-ray Analysis (EDX)

3.6.1 Introduction

When a finely focused electron beam impinges on the surface of a solid material it gives rise to an X-ray spectrum. From the quantum energy and intensity of the peaks in this spectrum the elements present may be identified and their concentration estimated with a spatial resolution of about 1 micrometer. By varying the energy of the primary electron beam, information from different levels (up to about 2 μm) in the specimen can be obtained.

The technique is applied widely and becomes more significant when combined with AES became a simultaneous surface and inner layer composition of sample can be obtained.

3.6.2 X-Ray Emission

Again, shown in Fig 3.1, X-ray emission line are produced by transitions between inner atomic electron energy levels. For such a transition to be possible a vacancy must be created by the ejection of an inner electron. In EDX, the required inner level ionisation is produced by bombardment with electrons of sufficient kinetic energy. Fig 3.19 (217), indicates some of the more common transitions between the K, L, M and N shells of an atom which lead to the X-ray lines. The quantum energy of the emitted radiation is equal to the difference between the potential energy of the atom in its initial and final states.

The energy of a particular line increases smoothly with the atomic
Fig. 3.19 Some of the more common transitions between the K, L, M and N shells of an atom which lead to the X-ray lines indicated (after Goodhew, (217))

Fig. 3.20 Schematic diagram of Si(Li) detector cryostat assembly (after Reed, (218))
number of the emitting atom, owing to the increasing binding energy of the inner levels and is uniquely characteristic of the emitting element.

For most purposes it may be assumed that the energy and intensity of characteristic lines are independent of the physical and chemical state of the emitter, since only inner energy levels are involved.

Electron bombardment generates not only characteristic X-ray line, but also a continuous spectrum, or 'bremsstrahlung', consisting of photos emitted by electrons suffering deceleration in collisions with atoms. The continuous spectrum extends up to a limiting energy equal to the incident electron energy.

The ionisation of an inner shell may be followed by a radiationless transition rather than one resulting in the emission of an X-ray photon. In this event the energy released in the transition is used to eject another electron from the atom. This is known as the Auger effect which has been mentioned in Section 3.2.2.

The relationship between the intensity of an X-ray line and the concentration of the element concerned depends in a complicated manner on the composition of the sample. 'Matrix correction' which depends on composition is used to convert specimen/standard intensity ratios into concentrations.

The phenomena upon which matrix corrections depend are:

(1) absorption of characteristic X-ray emerging from the specimen;
(2) enhancement of the characteristic X-ray intensity due to fluorescence by other lines and the continuum;
(3) loss of X-ray intensity owing to incident electrons being backscattered out of the specimen;
(4) variation in the efficiency of X-ray production, which is governed by the 'stopping power' of specimen (a function of atomic number).

The overall matrix correction factor $F$ is given by the product of above individual factors:

$$F = F_a \times F_p \times F_b \times F_s \quad (3-17)$$

In EDX, the effective spatial resolution depends on the spatial distribution of X-ray production in the analysed region. The X-ray source is roughly pear-shaped, with emission concentrated around the centre and falling off with distance from the point of impact of the electrons. Spatial resolution is related to the lateral X-ray distribution function, which is analogous to the depth distribution $\phi(p^\perp)$.

The depth distribution function $\phi(p^\perp)$ is known to be approximately independent of atomic number for a given incident electron energy. Reed (218) derived a general expression for resolution $d$ (in $\mu$m):

$$d = 0.077 \left( \frac{E_o^{1/3} - E_c^{1/3}}{\rho} \right) \quad (3-18)$$

where $E_o$ incident electron energy, keV

$E_c$ critical excitation energy, keV

$\rho$ density

3.6.3 Lithium Drifted Silicon Detector

The probe forming system and an X-ray detector are the main components of the EDX system. The most common X-ray detectors for EDX are solid state detectors, with such detectors the whole spectrum is recorded simultaneously and electronic pulse height analysis is used to sort the pulses produced in the detector, according to X-ray energy.

Lithium-drifted silicon detectors Si(Li) are widely used as solid state
X-ray detectors, and are schematically illustrated in Fig 3.20 (218).

The X-ray signal from the sample passes through the thin beryllium window before reaching the Si(Li) detector. The energy of X-rays incident on the detector is transferred to Auger and photoelectrons which dissipate their energy in the detector medium, generating charge carriers (electrons and holes) in the process. A bias voltage is applied so that the charge carriers move rapidly to the electrodes.

A field effect transistor (FET) is used as preamplifier because it offers the best signal to noise ratio. The signal pulses are further amplified by a main amplifier and fed into data system. A multichannel pulse height analyser is almost invariably used. This sorts the detector pulses according to their height, and hence X-ray energy, and records the number received in each channel (218).
3.7 MA500 Auger Lab

MA500 Auger Lab is a scanning Auger electron microscope manufactured by VG Scientific Ltd. U.K. It permits the acquisition simultaneously, of both the Auger electron and the X-ray signals excited by the electron beam from a given picture element. In fact, it is an electron probe microanalyzer working in two depth zones, and also has facilities for other surface study techniques, XPS, XRF (X-ray fluorescence spectroscopy), and an argon ion gun for surface profiling at samples. The picture of the machine and its physical arrangement are shown in Fig 3.21-23.

3.7.1 Microscope

Fig 3.24 schematically illustrates the construction of the MA500 microscope. This is a vertical, three lenses, scanning electron type. The electron gun permits working to 30kV. A conventional tungsten filament was used, but since August in 1987, a LaB$_6$ filament is used to obtain higher brightness.

There are two electromagnetic condenser lenses for reducing the electron beam diameter and an electromagnetic objective lens for focussing the probe sharply on the specimen.

The stigmator and the scanning coils are built into the objective lens. Apertures are placed in the column to control the beam. An externally adjustable final aperture blade is positioned at the final lens centre to control the spot size. A choice of three aperture or wide open can be obtained.
Fig 3.22 The arrangement of the MA500 instrument chambers
Fig. 3.23 The physical arrangement of the MA500 instrument
Fig. 3.24 Electromagnetically focused electron gun designed to produce beams of electrons of energies up to 30 keV. At beam currents of a few nanoamperes the optimum spot size on the specimen is about 50 nm (after Riviere, (202))

Fig. 3.25 Spatial distribution of sources and detectors in the MA500
The normal working distance is 2 cm and at this position the resolution in the SEM mode is 40 nm. To carry out analyses with reasonable counting statistics, the spatial resolution must be sacrificed. A general expression for resolution is given by:

\[ d = \frac{66}{i} \]  

(3-19)

where \( d \) = spot size, nm
\( i \) = beam current, nA

3.7.2 X-ray Source MkII (for XPS)

A twin anode (Al/Mg) type X-ray source is attached to the microscope to provide XPS. It is operated with the filament near earth potential and the anode at a positive potential of up to 15 kV.

3.7.3 Electron Energy Analyser

Electrons are detected via a transfer lens leading into a 10 cm concentric hemispherical analyser with a channeltron detector.

The principles of operation of the analyser have been mentioned in Section 3.1.3. Three different size slits are available to control the angular dispersion of electrons passing through the analyser and hence its resolution. The size of the slits are 2, 1, and 0.5 mm. The transfer lens serves to collimate a beam of Auger or photo-electrons which may then pass into the analyser at a low entrance angle. The lens has the additional advantage that it isolates the analyser from field associated with the column, and creates far more workspace around the specimen.

The analyser gives a measured resolution of 0.8 eV on the silver peak.
(pass energy 5 eV, 12000 counts at 300 W of Al Kα radiation). When analysing at 4 nA on an electrode surface a retard ratio of 10:1 is used, corresponding to an analyser resolution of 0.2% of the kinetic energy.

The analyser may be operated in either of two modes:

(1) Constant analyser energy (CAE)

As equation (3-7) shows \( K = R + E + W \), in CAE mode, pass energy \( E \) is fixed and \( R \) is scanned accordingly, allowing only electrons with energy \( E \) to pass through the analyser. This mode has the advantage of fixed resolution at all kinetic energies. At low kinetic energies, however, the sensitivity increases.

(2) Constant retard ratio (CRR)

The retard ratio, \( k \), is defined by

\[
 k = \frac{K-W}{E} \quad (\text{where } W = 4.2 \text{ eV})
\]  

(3-20)

In CRR mode, the ratio of kinetic to pass energy \( k \) is constant during a spectrum. Since \( E \) varies with \( K \) to keep a constant \( k \), a second voltage supply is used to ramp the hemispheres separately and with opposite polarity. The spectrometer control unit of MA500 allows retard ratios of 1, 2, 4, 10, 20, 50 and 100:1 to be selected either manually or via computer control. The sensitivity decreases at low energies.

In general the number of electrons ejected from a sample is greatest at low kinetic energies so that CAE tends to exaggerate this effect while CRR tends to counter it and produces a flatter background at low kinetic energies. The CAE mode is in general more useful for XPS and the CRR mode is more useful for AES.

3.7.4 X-Ray Detector (for EDX and XRF)
The X-ray system was supplied by Link systems (U.K) and is equipped with the sophisticated data acquisition system normally used for qualitative X-ray analysis.

A Si(Li) solid state X-ray detector is mounted at 45° to the electron detector and at 60° to the electron beam. It has an active area of 10 sq.mm and sensitive depth of 3 mm. The resolution is 158 eV FWHM at 5.9 keV. A 1 mm aperture is fitted in front of a Be window to reduce problems of detector saturation. The detector is demountable for instrument baking.

3.7.5 Argon Ion Source

The AG2 ion source, which has been described in Section 3.3.2, is mounted symmetrically to the X-ray detector on the other side of the electron detector. Fig 3.25 shows the relative geometry of the sources and detectors about the microscope column. This arrangement gives the least possible shadowing between Auger and X-ray signal on the other.

3.7.6 Acquisition and Presentation of Data

3.7.6.1 Data Acquisition

The collection of spectra and processing of data for AES, XPS, and EDX had been performed through Link Computer Series 860. (A Link AN10000 is used in the later) The computers have also been used to control retarding potential, ramp potential of analyser hemispheres and spectral collection time. The data acquisition can be organized effectively via 'Multi-Spec' Acquisition & Processing Software for the MA500 from Link Computer Co.
Fig. 3.26 Interface between the VG MA500 and the LINK 860
Fig 3.26 schematically shows the interface between the MA500 and the Link 860.

There are a variety of modes for data output including wide spectra which cover whole energies of interest, individual peak spectra and maps. Mapping offers a two dimensional data presentation of the entire area of interest of the sample surface.

The scan generator of the MA500 can be controlled externally by the Link computer, to enable digital acquisition and storage of scanning Auger images. X-ray data can be recorded simultaneously. Thus maps showing both surface (AES) and bulk (EDX) compositional features can be obtained from a given region of the sample.

The processed maps can be recorded directly by using a Polaroid SX-70 Land camera or a conventional camera. There are also facilities for transferring the spectral and map data from the Link computer storage to the Prime Computer of Surrey University for further data processing operations, such as representing maps of elemental concentration in contour or three dimensional form. The software for the extra facilities of data manipulation was prepared by Richardson (152).

3.7.6.2 Presentation of Data

(1) AES Data

AES spectra are either obtained from point analysis or TV analysis of the area concerned. As an example of the presentation of qualitative data, a full spectrum, Fig 3.27 (1) is labelled according to the peak position of the elements. The height of the peaks roughly indicates the amount of elements present in the surface. Another qualitative presentation of AES
Fig. 3.27 Examples of Auger and x-ray spectra
data is in the form of maps. The level of concentration of the elements present corresponds to different colours on the photograph of a map, or can be read from the contour lines of a contour map.

In order to eliminate topographical effects (220) which may affect the take-off angle and hence change in absorption of the emitted radiations, the data of the ratio of net peak height over background \((P-B)/B\), have been used to construct the maps.

(2) EDX Data

The EDX technique has only been used for qualitative analysis. Full X-ray spectra for energies from 0 to 10 keV, (Fig 3.27 (2)) have been used for presentation of EDX data. The height of the peaks indicates the amount of elements present deep below the surface of the sample. The x-ray maps have also been produced using the same routine as used in Auger mapping.

When producing a X-ray map for element Mn, the overlay of Cr \(K_p\) \((E = 5.946\ \text{keV})\) and Mn \(K_x\) \((E = 5.894\ \text{keV})\) must be considered. By measuring the heights of the peaks Cr \(K_x\) and Cr \(K_p\), for the type 316 stainless steel (not on the inclusion areas), the ratio of intensities of Cr \(K_x\) and Cr \(K_p\), \(R\), can be experimentally determined \((R \sim 5/1)\). After obtaining the map data for both Cr \(K_x\) and Cr \(K_p\) + Mn \(K_x\), the map of Mn \(K_x\) can be produced by deducting the intensity of Cr \(K_p\) \(\sim (1/R) \ast \text{intensity of Cr } K_x\) from the intensity of Cr \(K_p\) + Mn \(K_x\).

The \(K_p\) line of iron has been adopted for mapping because of the interference of Fe \(K_x\) line by the Mn \(K_p\) line.

For the purpose of this investigation both surface and bulk analytical techniques involving XPS, AES and EDX are adopted. Further more, the additional in-depth information obtained from the energy loss background of
photoelectron peaks is used to aid the understanding on the distribution of elements and ions in the passive films, which will be discussed in more detail in the next chapter.
Chapter 4

The Oxidation And Reduction Of Fe/Cr Alloy In The Oxygen At Low Partial Pressure And Vacuum:

the energy loss background of photoelectron peaks and its relationship to near-surface composition gradients

4.1 Introduction

It was shown in Chapter 2 that the passive films could be analysed by both XPS and AES. XPS also permits the analysis, at the same time, of the underlying metal since the spectra can be separated by means of the chemical shift. However, this is only satisfactory for films of the order of 2 nm in the thickness and cannot be used for Auger spectroscopy. In this chapter the use of supplementary means to obtain near-surface composition information from different preparations of passive films is described.

These supplemental means have been introduced in the previous chapter and include:

(1) Destructive argon ion etching;

(2) Non-destructive methods.

As a non-destructive method for obtaining a depth profile, the technique of angular resolved electron spectroscopy is used. Also the energy loss background (characterised by the P-PS, ELTH, or slope of base line) is utilized to aid the determination of the near surface distribution of elements and ions.
In this investigation the behaviour of an iron/chromium alloy, heated in vacuum or exposed in oxygen in different sequences, has been investigated using the methods reported earlier for single metals. The object of the study is to gain understanding of how the background depends on the layered structure of the oxide of iron and chromium within the oxide film. The argon ion sputtering technique and the angular profile were used to further confirm the results.

As a supplementary means, the post-peak energy loss structure (P-PS), the slope of base line of spectra, and the energy loss tail (ELTH) were used quantitatively to amplify the analytical results from XPS. The work demonstrated that energy loss structures on photoelectron peaks, which have generally been regarded as a nuisance, may provide useful secondary information on the depth distribution of near-surface elements and therefore enhance information available from XPS.
4.2 Experimental

4.2.1 Material and Specimen Preparation

The model steel was obtained as Cast 515 from Prof. Grabke of the Max-Plank Institute, Dusseldorf. The composition of this alloy is listed in Table 4.1.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.022</td>
<td>0.047</td>
<td>0.0054</td>
<td>0.004</td>
<td>0.0023</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Mo</th>
<th>Cr</th>
<th>Al</th>
<th>N</th>
<th>Fe</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;0.01</td>
<td>16.8</td>
<td>&lt;0.001</td>
<td>0.019</td>
<td>balance</td>
<td></td>
</tr>
</tbody>
</table>

The samples were wet ground on emery papers to 1200 grit, followed by polishing with diamond paste to 6 μm. The final polish was performed with 1 μm alumina on dry cloth to give a clean surface suitable for surface analysis, polishing was taken to a mirror finish.

Prior to mounting the specimens on the sample holder of ESCA3 MkII, the holder was outgassed by a preliminary heat cycle in the spectrometer vacuum. The heating was performed by a resistance heater in the probe tip.

The samples were cleaned for 1 minute by ion bombardment in the analyser chamber using argon which had been cleaned over hot titanium. The energy of the argon ion was 3 keV with a focussing voltage of 1.5 kV and a
residual pressure in the analyser chamber of 10^-6 Torr. These conditions give an etch rate of 0.62 nm/min (on Ta_2O_5 scale).

The temperature of the heated holder and specimens, was measured by a thermocouple in the probe and controlled by adjustment of the heater current.

4.2.2 Experimental Procedure

4.2.2.1 Heating in Vacuum (Experiment No 5153-)

After the outgassing of the sample holder, mounting of the specimen, and its cleaning by 1 minute argon ion bombardment the specimen was heated in the preparation chamber at 10^-9 ~ 10^-8 Torr vacuum and ~300°C for the desired lengths of time. Following each heating, the specimen was cooled to room temperature in vacuum and the XPS spectra were recorded. A survey spectrum together with high resolution regions of Fe 2p, Cr 2p, O 1s, C 1s, N 1s, and Ar 2p were recorded.

4.2.2.2 Heating in Vacuum — Depth Profile (No 5155-)

To obtain a compositional depth profile, the in-situ erosion of the sample surface by a beam of argon ions was used.

The cleaned specimen was heated at 4*10^-9 ~ 1*10^-7 Torr vacuum and ~300°C for 90 minutes. The argon ion bombardments were carried out for certain sputtering times repeatedly after the heated specimen was cooled to room temperature. The XPS spectra were recorded following heating and each etching.
4.2.2.3 Heating in Vacuum — Angular Profile (No 5158-)

Again, a specimen was heated in vacuum for 90 minutes, the XPS spectra were taken at electron take-off angles of 15°, 25°, 35°, 45° and 60° relative to the sample surface. A quantitative surface analysis could then be calculated for each take-off angle. The computer routine (206) mentioned in Section 3.4.2 was used to calculate a matching angular profile from a postulated depth profile.

4.2.2.4 Exposure in Oxygen — Heating in Vacuum (No 5156-) (No 5157-)

To grow some oxide on the surface, an oxygen flask was mounted on the preparation chamber so that the gas could be bled in as required through a leak valve. The cleaned sample was first exposed to 500, 1000, and 2000L of oxygen in sequence. During the oxidation, the oxygen level in the preparation chamber was $10^{-6}$ Torr and the temperature of the specimen was ~200°C. After each exposure, the specimen was cooled to room temperature at $10^{-1}$ Torr oxygen level and the chamber then evacuated. XPS spectra were recorded at a vacuum of $7 \times 10^{-9} - 5 \times 10^{-10}$ Torr.

After oxidation the specimen was heated in the preparation chamber at $2 \times 10^{-9} - 2 \times 10^{-7}$ Torr vacuum and ~300°C for various lengths of time, as shown in the Tables, interspersed by cooling in vacuum and recording the XPS spectra.
4.3 Peak Fitting

4.3.1 Peak Fitting Routine

The programme which we have used for curve-fitting in this work was developed by Laderer and modified by Baird and Richardson (152) and is run on the Prime 550 computer at the University of Surrey. This complex peak fitting programme is called GAMET.

Briefly, the curve fitting provided by this routine is accomplished using a non-linear least square method. The peaks fitted can be from 100% Gaussian to 100% Lorentzian in shape. Each of these peaks is further modified in shape by the addition of any subsidiary peaks induced by X-ray satellites in the exciting radiation. This is particularly essential for this work as the satellites of Cr 2p\(_{1/2}\) (Fe 2p\(_{3/2}\)) components occur under the Cr 2p\(_{3/2}\) (Fe 2p\(_{1/2}\)) envelope.

Another feature, which is provided, is the choice of the background tail following every predefined peak.

The tail can be fixed to be constant, exponential or the mixture of the two. The tail height relative to the peak height (%) is called the electron energy loss tail height, ELTH. The baseline slope and intercept can be fixed or left free to be calculated by the programme. This enables the variation of the background to be followed for each component in the spectrum envelope with some information about thickness and concentration of superficial layer.

Other parameters associated with each peak that can be fixed or left free are the position, the full width at half maximum, the intensity (having fixed the intensity the intensity ratio of two peaks can also be
fixed) and the separation from other peaks in the spectrum. One further variable sets a limit on the number of channels by which the programme can move peaks during fitting.

Once the estimated peaks have been assigned, the programme calculates all the peaks iteratively and fits them to the measured spectrum. The calculation is terminated either

(1) after all input parameters have been fitted to the best fit, or
(2) after the maximum preset number of iterations, which is 25, has been reached.

The calculated spectrum is built as an integral of all fitted peaks and their tails. The calculated spectrum is matched to the measured spectrum. The quality of the fit is determined by the value of the $X^2$ (chi-squared) which is given by

$$X^2 \text{ (calc)} = \sum_{i=1}^{n} \frac{[Y_i(\text{meas}) - Y_i(\text{calc})]^2}{Y_i(\text{calc})}$$

where $Y(\text{meas})$ = the experimental count rate

$Y(\text{calc})$ = the curve fitted count rate

$n$ = the number of points in the fitted region of the spectrum

For effective use of GAMET it is important to minimise the number of free variables. In this work, the same spectrometer analyser energy (50eV) is used for all peaks. This gives a good signal to noise ratio, but it governs also the analyser broadening which is Gaussian and sufficiently wide that 100% Gaussian peaks can be used for peak fitting.

Before the fitting routine can be run an input data file has to be prepared by a dialogue between the user and computer. This data file contains the raw data to be fitted, the peak guesses with which the fitting starts, and a complex set of variables which control the way in which the
programme can modify the peak parameters during fitting. After the input
data file has been set up, it can still be accessed to modify the estimates
of peak parameters, before it is read into the fitting routine.

After the fitting process is completed, an output file called GOUT.xx is
obtained, where xx represents the code for the terminal used in the curve
fitting. This file can be accessed for editing or obtaining a hard-copy.
The plot of the fitted spectrum is kept in a plotfile called PLOT.xx, which
includes a selected number of fitted parameters such as peak positions,
widths, areas and percentages. The hard-copy of this plotfile can be
obtained by spooling it to the University CALCOMP drum-plotter or by
plotting it using the Hewlett Packard Plotter located alongside the
terminal.

4.3.2 Peak Fitting of Chromium 2p

Using the programme described in Section 4.3.1 peak fitting of the
chromium 2p doublet is carried out over the range 569-593 eV. Both Cr
2p₃/₂ and 2p₁/₂ were fitted in order to estimate quantitatively Cr(0) and
Cr(III) and to calculate the contribution of Kα₃,₄ satellite of 2p₁/₂ which
overlaps with 2p₃/₂ peaks.

The fitting peak was of Gaussian shape and had a constant intensity
tail as shown in Fig 4.1. The slope of the base line used during the peak
fitting was allowed to vary in order to get a 'good fit'. The details and
the physical meaning of the varying slope will be mentioned in Section 4.4
and 4.5.

The ratio of 2p₃/₂ : 2p₁/₂ for components Cr(0) and Cr(III) is expected
to be 2:1, according to theoretical considerations. The results of Cr peak
Fig 4.1 Four-peak fitting of Cr 2p spectrum with Gaussian shape and constant intensity tail.
fitting in this work are basically consistent with this expectation and in agreement with the previous work of this laboratory (152, 215, 216).

4.3.3 Peak Fitting of Iron 2p

The iron 2p doublet has been fitted over the range 702-740 eV, to include both the $2p_{3/2}$ and $2p_{1/2}$ peaks. Again, the Gaussian shape, constant intensity tail and varying slope of base line were adopted.

During the peak fitting of Fe 2p doublet in the earlier stage in this work, the peaks for Fe(0), Fe(II), Fe(III) and one combined satellite peak for both Fe(II) and Fe(III) were placed for $2p_{3/2}$ and $2p_{1/2}$ respectively. Because of the presence of the various satellite structures within the iron spectra as the various chemical states, the peak widths of the satellites and the ratio between the major and satellite peaks changed when the concentrations of components changed, which also leads to the ratio of $2p_{3/2}$ and $2p_{1/2}$ to depart from 2:1. see Fig 4.2.

A deeper understanding of Fe spectra is the essence of obtaining a good fit. Both Fe(II) and Fe(III) possess their respective two satellites, as do those of some transition metals such as Cu, Ni (220) and both need to be considered. This fact means that 14 peak positions are needed for fitting Fe 2p doublet — two for Fe(0), six for Fe(II), and six for Fe(III). The present GAMET programme, however, provides only 8 peak positions. Thus an attempt had to be made to partly fit them within the limited number of peak positions available for these spectra of oxides which showed evidence of more than one valence state.

An attempt was made to find the correct positions of satellites and the proper ratios of major peaks and satellites to get 'good fit', by fitting
Fig 4.2 Eight-peak fitting of Fe 2p spectrum

The ELTH changes for both metallic iron and its oxide caused by vacuum annealing
the standard samples of the ferric and ferrous oxide over the range 702-726 eV, which contains all peaks of \(2p_{3/2}\) including the major peak and two satellites and major peak of \(2p_{1/2}\). Further, 'good fits' have been obtained from the spectra recorded from treated Cast 515 steel, using the peak positions and the ratio of peaks obtained from standard sample.

The pure \(\text{Fe}_2\text{O}_3\) sample was obtained by heating pure iron (Grade 1 iron sheet) in oxygen at 1000°C for 48 hours. The Fe 2p spectrum was recorded and fitted, shown in Fig 4.3.

<table>
<thead>
<tr>
<th></th>
<th>(\text{Fe(III) 2p}_{3/2})</th>
<th>(\text{Fe(III) 2p}_{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Major peak})</td>
<td>711.7</td>
<td>725.1</td>
</tr>
<tr>
<td>(\text{Satellite-1})</td>
<td>714.7</td>
<td>100</td>
</tr>
<tr>
<td>(\text{Satellite-2})</td>
<td>720.1</td>
<td>10.58</td>
</tr>
<tr>
<td>Area Ratio to (2p_{3/2}) major peak %</td>
<td>100</td>
<td>10.58</td>
</tr>
</tbody>
</table>

(The binding energy of carbon was 285.6 eV)

For the ferrous oxide,

<table>
<thead>
<tr>
<th></th>
<th>(\text{Fe(II) 2p}_{3/2})</th>
<th>(\text{Fe(II) 2p}_{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Major peak})</td>
<td>709.4</td>
<td>723.3</td>
</tr>
<tr>
<td>(\text{Satellite-1})</td>
<td>711.8</td>
<td>100</td>
</tr>
<tr>
<td>(\text{Satellite-2})</td>
<td>715.0</td>
<td>19.80</td>
</tr>
<tr>
<td>Area Ratio to (2p_{3/2}) major peak %</td>
<td>100</td>
<td>19.80</td>
</tr>
</tbody>
</table>

(The carbon peak position was 284.2 eV)

Fig 4.4 shows an example to fit the spectra which includes both Fe(II) and Fe(III) by using the positions and the area ratios obtained from the standard specimens.
Fig 4.3 Peak fitting of the Fe spectrum recorded from pure Fe₂O₃.
Fig 4.4 An example to fit the spectra by using the positions and the area ratios obtained from the standard specimens.
4.4 Results

4.4.1 Heating in Vacuum (No 5153-)

The sample was heated in vacuum and the spectra were recorded using the procedure described above.

The spectrum of each treatment was analysed as shown in Table 4.2.

Clearly, 1 minute's etching removed the carbon contamination on the surface, but did not change the Fe/Cr ratio. When the specimen was further heated for 20 minutes and cooled, the carbon contamination increased again, but there was also a change in the Fe/Cr ratio. Annealing decreased the ratio implying the enrichment of chromium on the surface.

Table 4.2

<table>
<thead>
<tr>
<th>No</th>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Ar</th>
<th>Fe/Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>5153A</td>
<td>Original</td>
<td>10.4</td>
<td>3.9</td>
<td>40.7</td>
<td>44.8</td>
<td>0.24</td>
<td>2.67</td>
<td></td>
</tr>
<tr>
<td>5153B</td>
<td>Etch 1 min</td>
<td>19.4</td>
<td>7.1</td>
<td>21.3</td>
<td>50.6</td>
<td>0.52</td>
<td>1.10</td>
<td>2.73</td>
</tr>
<tr>
<td>5153C</td>
<td>Heat 20 mins</td>
<td>13.4</td>
<td>6.0</td>
<td>36.5</td>
<td>43.3</td>
<td>0.38</td>
<td>0.50</td>
<td>2.23</td>
</tr>
<tr>
<td>5153D</td>
<td>+ 30 mins</td>
<td>13.1</td>
<td>5.9</td>
<td>38.4</td>
<td>41.4</td>
<td>0.76</td>
<td>0.46</td>
<td>2.22</td>
</tr>
<tr>
<td>5153E</td>
<td>+ 30 mins</td>
<td>13.9</td>
<td>6.3</td>
<td>37.6</td>
<td>41.2</td>
<td>0.64</td>
<td>0.40</td>
<td>2.21</td>
</tr>
</tbody>
</table>
Due to the higher affinity of chromium for oxygen and the absence of oxygen in spectrometer vacuum, chromium diffused from substrate towards the surface to reduce the oxide of iron. As a result, a new overlayer which is more rich in Cr$_2$O$_3$ formed near the surface. Therefore, the photoelectrons emitted from the iron located under this overlayer have to undergo more inelastic collisions during their passage across the overlayer. In other words, the background tail of iron spectrum should increase. This is illustrated in Fig 4.5 which shows a group of spectra of iron.

5153 A, is for original polished surface;
5153 B, is for the cleaned surface. The removal of carbon and the part of passive film obviously decreased the tail height;
5153 C, shows the tail of spectrum goes up again, after the annealing. The difference on the tail height is much more obvious than that of the ratio of Fe/Cr which obtained from traditional surface analyses, as shown in Table 4.2. To study quantitatively these chemical changes in the surface composition and their relation to energy loss structure seen in XPS, peak fitting was needed.

By fitting the Fe 2p and Cr 2p spectra, the area percentages of different valence states (Fe(0), Fe(II), Fe(III) and Cr(0), Cr(III)) were obtained and shown in Table 4.3, 4.4. The values in Table 4.3 are the results of normalizing the areas of Fe(0), (II), and (III) for 2p$_{3/2}$. 

Fig 4.1 and 4.2 give samples of spectra fitted in this way.

One minutes etching partly stripped the oxide of iron (Fe$_2$O$_3$) on the surface so that the Fe(0) and Fe(II) increased, Table 4.3.

When the cleaned sample was heated in vacuum, again, Fe(0) and Fe(II) increased, while the Fe(III) decreased. Considering the decrease of Cr(0)
Fig 4.5 XPS spectra of Fe 2p showing the dependence of the spectrum tail on surface treatment

S1S3A, for the original polished surface;

S1S3B, for the surface cleaned by 1 minute argon etching;

S1S3C, for the surface after 20 minute vacuum annealing.
### Table 4.3

<table>
<thead>
<tr>
<th>No</th>
<th>Fe(0)</th>
<th>Fe(II)</th>
<th>Fe(III)</th>
<th>Fe(0)</th>
<th>Fe(II+III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5153A Original</td>
<td>5.09</td>
<td>62.26</td>
<td>32.65</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>5153B Etch 1 min</td>
<td>6.61</td>
<td>72.68</td>
<td>20.71</td>
<td>0.44</td>
<td>0.24</td>
</tr>
<tr>
<td>5153C Heat 20 mins</td>
<td>8.23</td>
<td>79.28</td>
<td>12.49</td>
<td>0.45</td>
<td>0.38</td>
</tr>
<tr>
<td>5153D + 30 mins</td>
<td>8.26</td>
<td>80.95</td>
<td>10.79</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>5153E + 30 mins</td>
<td>9.28</td>
<td>81.40</td>
<td>9.32</td>
<td>0.46</td>
<td>0.45</td>
</tr>
</tbody>
</table>

### Table 4.4

<table>
<thead>
<tr>
<th>No</th>
<th>Cr(O) 2p3/2</th>
<th>Cr(O) 2p1/2</th>
<th>Cr(III) 2p3/2</th>
<th>Cr(III) 2p1/2</th>
<th>Cr(O)</th>
<th>Cr(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5153A Original</td>
<td>3.94</td>
<td>1.98</td>
<td>64.22</td>
<td>29.87</td>
<td>0.50</td>
<td>0.22</td>
</tr>
<tr>
<td>5153B Etch 1 min</td>
<td>1.90</td>
<td>0.94</td>
<td>65.36</td>
<td>31.79</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>5153C Heat 20 mins</td>
<td>1.52</td>
<td>0.76</td>
<td>64.00</td>
<td>33.72</td>
<td>0.48</td>
<td>0.26</td>
</tr>
<tr>
<td>5153D + 30 mins</td>
<td>0.81</td>
<td>0.41</td>
<td>64.64</td>
<td>34.14</td>
<td>0.44</td>
<td>0.26</td>
</tr>
<tr>
<td>5153E + 30 mins</td>
<td>0.45</td>
<td>0.23</td>
<td>65.46</td>
<td>33.82</td>
<td>0.28</td>
<td>0.28</td>
</tr>
</tbody>
</table>
at the same time, Table 4.4, confirmed that the chromium in Cast 515 steel diffused from the substrate to surface and was oxidized to \( \text{Cr}_2\text{O}_3 \), by reduction of the oxide of iron.

As Table 4.3 shows, the ELTH for both metallic iron and its oxide increased with annealing time. The ELTH of the oxide increased more than those of metallic iron. Fig 4.2 shows this change too. After heating for 20 minutes and then another 20 minutes, the ELTH changed from 44% for Fe(0) to 45%, 24% for Fe(II) and Fe(III) (5153B) to 45% (5153D).

Note that the difference of ELTH for Fe(0) and Fe(II+III) of the cleaned specimen reveals the presence of a very thin oxide film of iron before heating the specimen in vacuum.

4.4.2 Heating in Vacuum — Depth profile (No 5155–)

At first the specimen was heated in vacuum for 90 minutes, then the argon ion gun was used to obtain the in-depth distribution of chemical composition. The composition, as a function of sputtering time, is shown in Table 4.5. To remove the influence of carbon, the concentration, for oxygen, iron and chromium was normalized and the results are shown in Table 4.6 and Fig 4.6.

The results confirmed those in Section 4.4.1. After 90 minutes' annealing, the region near the surface is richer in chromium. As the sputtering time increased so the concentration of Cr decreased. Conversely, the content of Fe and ratio Fe/Cr obviously increased.

Again, by fitting the spectra of Fe and Cr, the areas of peaks and tail heights of different components are given in Table 4.7 and 4.8.
Table 4.5

<table>
<thead>
<tr>
<th>No</th>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Ar</th>
<th>Fe/Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>5155A</td>
<td>Original</td>
<td>9.4</td>
<td>4.8</td>
<td>32.3</td>
<td>53.3</td>
<td>0.27</td>
<td>-</td>
<td>1.96</td>
</tr>
<tr>
<td>5155B</td>
<td>Heat 90 mins</td>
<td>11.4</td>
<td>13.9</td>
<td>31.6</td>
<td>42.8</td>
<td>0.31</td>
<td>-</td>
<td>0.82</td>
</tr>
<tr>
<td>5155C</td>
<td>Etch 0.5 mins</td>
<td>14.2</td>
<td>16.2</td>
<td>21.2</td>
<td>47.2</td>
<td>0.29</td>
<td>0.99</td>
<td>0.88</td>
</tr>
<tr>
<td>5155D</td>
<td>Etch 1.0 mins</td>
<td>16.2</td>
<td>16.0</td>
<td>19.1</td>
<td>47.0</td>
<td>0.34</td>
<td>1.3</td>
<td>1.01</td>
</tr>
<tr>
<td>5155E</td>
<td>Etch 1.5 mins</td>
<td>17.4</td>
<td>16.2</td>
<td>19.1</td>
<td>45.5</td>
<td>0.49</td>
<td>1.2</td>
<td>1.07</td>
</tr>
<tr>
<td>5155F</td>
<td>Etch 2.0 mins</td>
<td>16.4</td>
<td>14.7</td>
<td>24.8</td>
<td>42.6</td>
<td>0.40</td>
<td>1.2</td>
<td>1.12</td>
</tr>
<tr>
<td>5155G</td>
<td>Etch 3.0 mins</td>
<td>23.4</td>
<td>14.4</td>
<td>20.8</td>
<td>39.3</td>
<td>0.56</td>
<td>1.5</td>
<td>1.63</td>
</tr>
<tr>
<td>5155H</td>
<td>Etch 4.0 mins</td>
<td>24.8</td>
<td>12.6</td>
<td>21.2</td>
<td>39.4</td>
<td>0.52</td>
<td>1.5</td>
<td>1.97</td>
</tr>
<tr>
<td>5155I</td>
<td>Etch 6.0 mins</td>
<td>30.4</td>
<td>12.7</td>
<td>21.0</td>
<td>33.8</td>
<td>0.40</td>
<td>1.8</td>
<td>2.39</td>
</tr>
</tbody>
</table>
Table 4.6

\[ \sum (O + Fe + Cr) = 100\% \]

<table>
<thead>
<tr>
<th>No</th>
<th>O</th>
<th>Fe</th>
<th>Cr</th>
<th>Fe/Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>5155A</td>
<td>Original</td>
<td>78.81</td>
<td>13.93</td>
<td>7.26</td>
</tr>
<tr>
<td>5155B</td>
<td>Heat 90 mins</td>
<td>62.85</td>
<td>20.41</td>
<td>0.82</td>
</tr>
<tr>
<td>5155C</td>
<td>Etch 0.5 mins</td>
<td>60.82</td>
<td>18.30</td>
<td>20.88</td>
</tr>
<tr>
<td>5155D</td>
<td>Etch 1.0 mins</td>
<td>59.35</td>
<td>20.45</td>
<td>20.20</td>
</tr>
<tr>
<td>5155E</td>
<td>Etch 1.5 mins</td>
<td>57.52</td>
<td>22.00</td>
<td>20.48</td>
</tr>
<tr>
<td>5155F</td>
<td>Etch 2.0 mins</td>
<td>57.80</td>
<td>22.25</td>
<td>19.95</td>
</tr>
<tr>
<td>5155G</td>
<td>Etch 3.0 mins</td>
<td>52.97</td>
<td>30.35</td>
<td>16.68</td>
</tr>
<tr>
<td>5155H</td>
<td>Etch 4.0 mins</td>
<td>51.30</td>
<td>32.29</td>
<td>16.41</td>
</tr>
<tr>
<td>5155I</td>
<td>Etch 6.0 mins</td>
<td>43.96</td>
<td>39.53</td>
<td>16.51</td>
</tr>
</tbody>
</table>
Fig. 4.6 In-depth distribution of chemical composition of 515 specimen annealed in vacuum for 90 minutes. Concentration of Fe, Cr and Fe/Cr ratio, as a function of sputtering time.

\[(O + Fe + Cr) = 100\%\]

- **O** = Fe
- **x** = Cr
- **Δ** = Fe/Cr

Etch time (minutes) \(\times 10^{-1}\)
<table>
<thead>
<tr>
<th>No</th>
<th>Fe(0)</th>
<th>Fe(II)</th>
<th>Fe(III)</th>
<th>Fe(0)</th>
<th>Fe(II+III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5155A Original</td>
<td>10.73</td>
<td>78.58</td>
<td>10.69</td>
<td>0.52</td>
<td>0.46</td>
</tr>
<tr>
<td>5155B Heat 90 mins</td>
<td>26.91</td>
<td>63.66</td>
<td>9.43</td>
<td>0.52</td>
<td>0.37</td>
</tr>
<tr>
<td>5155C Etch 0.5 mins</td>
<td>30.23</td>
<td>59.03</td>
<td>10.75</td>
<td>0.54</td>
<td>0.26</td>
</tr>
<tr>
<td>5155D Etch 1.0 mins</td>
<td>42.47</td>
<td>50.45</td>
<td>7.08</td>
<td>0.58</td>
<td>0.15</td>
</tr>
<tr>
<td>5155E Etch 1.5 mins</td>
<td>50.84</td>
<td>46.22</td>
<td>2.94</td>
<td>0.57</td>
<td>0.15</td>
</tr>
<tr>
<td>5155F Etch 2.0 mins</td>
<td>54.52</td>
<td>42.41</td>
<td>3.07</td>
<td>0.58</td>
<td>0.07</td>
</tr>
<tr>
<td>5155G Etch 3.0 mins</td>
<td>60.96</td>
<td>35.01</td>
<td>4.03</td>
<td>0.48</td>
<td>0.10</td>
</tr>
<tr>
<td>5155H Etch 4.0 mins</td>
<td>63.28</td>
<td>33.10</td>
<td>3.62</td>
<td>0.41</td>
<td>0.10</td>
</tr>
<tr>
<td>5155I Etch 5.0 mins</td>
<td>63.63</td>
<td>30.16</td>
<td>6.21</td>
<td>0.36</td>
<td>0.07</td>
</tr>
<tr>
<td>No</td>
<td>Condition</td>
<td>Area %</td>
<td>ELTH</td>
<td>slope</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2p$_{3/2}$</td>
<td>2p$_{1/2}$</td>
<td>2p$_{3/2}$</td>
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<td>Heat 90 mins</td>
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<td>3.58</td>
<td>60.37</td>
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</tr>
<tr>
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<td>Etch 0.5 mins</td>
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<td>57.62</td>
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<td>28.02</td>
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<tr>
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<td>5155H</td>
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<td>45.97</td>
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<td>Etch 6.0 mins</td>
<td>26.17</td>
<td>11.33</td>
<td>40.92</td>
<td>21.58</td>
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</table>
Fig 4.7 The quality improvement of fit by using a sloping base line
Spectrum of Cr 2p obtained from the specimen annealed in vacuum for 90 minutes followed by 1 minute argon etching
A. Fitted using a horizontal base line
B. Fitted using a downward inclined base line
When fitting the chromium spectra, it was very difficult to obtain a 'good fit' when the value '0' was determined as the slope of base line (i.e. if it was horizontal) for those spectra recorded after heating the specimen in vacuum. Fig 4.7.A shows such example of a 'bad fit' of 5155D.6. When the slope was changed from '0' to various positive values, i.e. to select downward inclined lines, better fits can be achieved for such spectra. Table 4.8 shows the results obtained by selecting 900 counts/eV as the slopes of base line, and it is very noticeable from Fig 4.7.B that the slope change from '0' to '900' greatly improved the quality of the fit.

4.4.3 Heating in Vacuum — Angular Profile (No 5158—)

To further confirm the results of 5153 and 5155, a series of angular experiments have been carried out as described in Section 4.2.2.3. The composition of the surface for various take-off angles θ is shown in Table 4.9. The composition for elements carbon, oxygen, iron and chromium was normalized to simplify the calculation, Table 4.10.A.

By using the computer routine mentioned in Section 3.4.2, two composition depth profiles are obtained, Table 4.10.B and 4.10.C, from which the calculated angular profiles are obtained and showed close agreement with the experimental angular profile in Table 4.10.A.

Fig 4.8.A, 4.8.B, and 4.8.C respectively present the experimental and calculated angular profiles as well as depth profiles for the two models. It can be seen that the agreement is fairly good for both postulated depth profiles, and thus the changes in composition at depths of greater than 24Å make little difference to the angular profile.
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<tr>
<th>No</th>
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<th>C</th>
<th>O</th>
<th>N</th>
<th>Fe/Cr</th>
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<td>45.6</td>
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<td>2.22</td>
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<td>Heat 90 mins</td>
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<td>12.8</td>
<td>50.2</td>
<td>24.8</td>
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<td>0.92</td>
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<td>0.84</td>
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### Table 4.10

#### A. Experiment

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<th>Cr</th>
<th>Fe</th>
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<td>26.95</td>
<td>15.23</td>
<td>12.73</td>
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<td>11.10</td>
<td>10.30</td>
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#### B. Calculation 1

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<th>Cr</th>
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#### Depth Å

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Table 4.10

C. Calculation

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Depth Å

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FIG. 4.8 (A) 5150 EXPERIMENTAL ANGULAR PROFILE
FIG 4.8 (B) MODEL 1
TOP POSTULATED DEPTH PROFILE
BOTTOM CALCULATED ANGULAR PROFILE
FIG. 4.8 (C) MODEL 2
TOP POSTULATED DEPTH PROFILE
BOTTOM CALCULATED ANGULAR PROFILE
The results of fitting of Fe spectra of the angular experiments are given in Table 4.11.A. The proportion of Fe(O) in the Fe spectrum envelope increased with increase of take-off angle, because the composition information involves deeper levels. For the fixed thickness of the Cr rich oxide overlayer, however, the photoelectrons emitted from the iron should pass a shorter effective depth within this overlayer as the take-off angle increased. Therefore, the tail heights (ELTH) of both Fe(O) and Fe(II+III) decreased. This conformed with the observation of ELTH in the 5153 series of experiments above. Similarly, the ELTH of Cr(O) also decreased with the increase of take-off angle, see Table 4.12.

It was difficult to achieve a good fit for the Cr and Fe spectra after heating, as had taken place in 5155 series. Again, the non-horizontal base lines with various values of slope were adopted in the curve fitting of Cr and Fe spectra to improve the quality of the fit, i.e. to obtain a small CHI SQ value and converged fit (shown by the number at the top right hand side of the graphical output is 1). Table 4.11.B and 4.12 show these results respectively for Fe and Cr.

Comparing the CHI SQ available and convergents in the Table 4.11.A and 4.11.B, it is certain that a great improvement in the fit quality has been achieved through changing the slope. Fig 4.9 (for Fe) and Fig 4.10 (for Cr) provided the examples of such improvements.
Fig 4.9 The quality improvement of fit by using a sloping base line
Spectrum of Fe 2p obtained from the specimen annealed in vacuum for 90 minutes using 15° take-off angle
A. Fitted using a horizontal base line
B. Fitted using an upward inclined base line
Fig 4.10 Spectrum of Cr 2p obtained from the specimen annealed in vacuum for 90 minutes using 35° take-off angle
A. Fitted using a horizontal base line
B. Fitted using a downward inclined base line
### Table 4.11 A

<table>
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<th>Area %</th>
<th>ELTH</th>
<th>Slope</th>
<th>CHI, SQ</th>
<th>Convergence</th>
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<td>9.70</td>
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<td>0</td>
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<td>8.50</td>
<td>0.54</td>
<td>0.38</td>
<td>0</td>
<td>953</td>
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### Table 4.11 B

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<th>Fe(II)</th>
<th>Fe(III)</th>
<th>Area %</th>
<th>ELTH</th>
<th>Slope</th>
<th>CHI, SQ</th>
<th>Convergence</th>
</tr>
</thead>
<tbody>
<tr>
<td>5158A</td>
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<td>0.32</td>
<td>-20</td>
<td>939</td>
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</table>
It is very noticeable from these tables that:

(1) In the case of iron, the better fits were achieved when the slopes were negative (upward inclined base line) and the absolute values of the slope decreased from 60 to 20 counts/eV as the take-off angle $\theta$ changed from 15° to 60°.

(2) In the case of chromium, however, the better fits were obtained when the slopes were positive (downward inclined base line) and the absolute values increased from 50 to 900 counts/eV as the take-off angle $\theta$ changed from 15° to 60°.
4.4.4 Exposing in O₂ — Heating in Vacuum
(No 5156—) (No 5157—)

The specimen was prepared and tests were carried out using the procedure described in Section 4.2.2.4. The survey spectra obtained during the oxidation and vacuum annealing are shown in Fig 4.11 A and B, and with the results of surface analysis shown in Table 4.13. The change of ratio of Fe/Cr as the function of exposing oxygen amount and heating time is shown in Fig 4.12.

To further illustrate the chemical change of the region near the surface, some high resolution spectra of the Fe 2p region recorded in the various steps were compiled in Fig 4.13. The slopes of post-peak range for the exposing experiments were calculated over a range of 25 eV beyond the Cr and Fe peaks, see Fig 4.14 and Table 4.14.

Table 4.13

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<th>80 mins</th>
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<td>C</td>
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Heat in vacuum

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<td>C</td>
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(A) 5156 OXIDATION

(C) 5157 ANNEALING IN VACUUM

Fig. 4.11
Fig. 4.12 (a) The ratio of Fe/Cr as a function of oxygen exposure

(b) The ratio of Fe/Cr as a function of vacuum annealing time
Fig 4.13 High resolution spectra of Fe 2p region recorded in the various steps:

- 5156A, clean surface
- 5156E, Exposure oxygen 500 L
- 5157C, Annealing in vacuum 50 minutes after exposure O₂ 2000 L
Fig 4.14 The slopes of post-peak calculated over a range of 25 eV beyond the Cr and Fe peaks
Table 4.14

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<tr>
<td>5156G 1000LO₂</td>
<td>-60.93</td>
<td>-12.60</td>
</tr>
<tr>
<td>5156I 2000LO₂</td>
<td>-3.01</td>
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4.4.5 Various Surface Conditions from Different Preparations of Film

So far, the formation of passive oxide film formed in-situ (or ex-situ) in different preparation of 515 alloy has been investigated. Table 4.15 (A, B, C) can be used as a summary, and shows the surface conditions for every type of treatment investigated.

A one minute etch for surface cleaning did not essentially change the ratio of Fe/Cr, even though some oxide was removed. As mentioned before, the oxidation increased this ratio, and the latter annealing in vacuum decreased it. Annealing in vacuum, without pre-oxidation, decreased the ratio greatly because Cr diffused toward to the surface and reduced the iron oxide, forming a layer which is rich in Cr.
For the shapes of the Fe 2p peaks, the table shows:

On polished and cleaned surfaces, the metallic iron shoulder is obvious, and both Fe(II) and Fe(III) satellites can been seen, but not clearly. That means the presence of a mixture of three chemical states of iron.

After oxidation, all spectra clearly show Fe(III). After further annealing, Fe$_2$O$_3$ was reduced to stable ferrous iron by the solid state reaction with chromium.

After annealing in vacuum without pre-oxidation, the metallic iron shoulder became clear as time increased, and Fe(II) satellites appeared.

Considering the chemical states of iron and the shapes of carbon and oxygen peaks in the high resolution spectra, the probable models for various surfaces are listed in the last column of Table 4.15.C.
<table>
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<tr>
<th>Type of surface</th>
<th>No</th>
<th>$\Sigma (O+Fe+Cr)$</th>
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<tr>
<td></td>
<td></td>
<td>%</td>
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<td>5153B</td>
<td>77.1</td>
<td>65.63</td>
</tr>
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<td>64.95</td>
</tr>
<tr>
<td></td>
<td>5156E 500L</td>
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</tr>
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<td>79.54</td>
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<td>5157A 20 min</td>
<td>60.4</td>
<td>64.57</td>
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<tr>
<td></td>
<td>5157C 50 min</td>
<td>61.2</td>
<td>63.56</td>
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<tr>
<td>after oxidation</td>
<td>5157E 80 min</td>
<td>58.3</td>
<td>64.00</td>
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<tr>
<td></td>
<td>5157G 120 min</td>
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<td>64.78</td>
</tr>
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<tr>
<td>Type of surface</td>
<td>No</td>
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<td>chemical state of iron</td>
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<td>-----</td>
<td>----------------</td>
<td>-----------------------</td>
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<td>Fe(O) satellite</td>
<td>Fe(II) Fe(III)</td>
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<tr>
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<td>+</td>
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<td>Etch 1 min</td>
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<td>++</td>
<td>+</td>
</tr>
<tr>
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<td></td>
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<tr>
<td></td>
<td>5156G</td>
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<td>++</td>
</tr>
<tr>
<td>in vacuum</td>
<td>20 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5157C</td>
<td>-</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td>50 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>after oxidation</td>
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<td>-</td>
<td>++</td>
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<td>80 min</td>
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</tr>
<tr>
<td></td>
<td>5157G</td>
<td>-</td>
<td>+++</td>
</tr>
<tr>
<td></td>
<td>120 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealing</td>
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<td>+</td>
<td>++</td>
</tr>
<tr>
<td>in vacuum</td>
<td>20 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5155B</td>
<td>+++</td>
<td>++</td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
<td>5158E</td>
<td>+++</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td>90 min</td>
<td></td>
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Table 4.15 (C)

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<th>Type of surface</th>
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<th>Width (eV)</th>
<th>O\textsubscript{1s}</th>
<th>C\textsubscript{1s}</th>
<th>Probable Model</th>
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<tr>
<td>Polished</td>
<td>5153A</td>
<td>3.5</td>
<td>OH\textsuperscript{-}</td>
<td>-C-C-</td>
<td>OH \rightarrow -C-C- \rightarrow C=O \rightarrow C-OH</td>
</tr>
<tr>
<td>surface</td>
<td>5155A</td>
<td>3.9</td>
<td>O\textsuperscript{2-}</td>
<td>(-C-OH)</td>
<td>-C-C- \rightarrow Cr\textsubscript{2}O\textsubscript{3} CrOOH (Fe\textsuperscript{2+} Fe\textsubscript{x}O\textsubscript{y} FeOOH)</td>
</tr>
<tr>
<td>surface</td>
<td>5158A</td>
<td>3.5</td>
<td>H\textsubscript{2}O OH</td>
<td>-C=H</td>
<td>+ Fe-Cr</td>
</tr>
<tr>
<td>Clean</td>
<td>5153B</td>
<td>2.7</td>
<td>O\textsuperscript{2-}</td>
<td>-C-C-</td>
<td>-C-C- \rightarrow Cr\textsubscript{2}O\textsubscript{3} CrOOH (Fe\textsuperscript{2+} Fe\textsubscript{x}O\textsubscript{y} FeOOH)</td>
</tr>
<tr>
<td>Etch 1 min</td>
<td>5156A</td>
<td>2.7</td>
<td>(OH\textsuperscript{-})</td>
<td>-C-C-</td>
<td>+ Fe-Cr</td>
</tr>
<tr>
<td>Oxidation</td>
<td>5156E</td>
<td>2.9</td>
<td>OH\textsuperscript{-}</td>
<td>-C-C-</td>
<td>OH \rightarrow -C-C- \rightarrow C=O \rightarrow C-OH</td>
</tr>
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<td>Oxidation</td>
<td>5156G</td>
<td>2.9</td>
<td>O\textsuperscript{2-}</td>
<td>(-C-OH)</td>
<td>+ Fe\textsubscript{2}O\textsubscript{3} FeOOH (Cr\textsubscript{2}O\textsubscript{3} CrOOH)</td>
</tr>
<tr>
<td>Oxidation</td>
<td>5156I</td>
<td>2.9</td>
<td>OH</td>
<td>-C-H</td>
<td>+ Cr\textsubscript{2}O\textsubscript{3} (Fe\textsubscript{x}O\textsubscript{y})</td>
</tr>
<tr>
<td>Annealing in vacuum</td>
<td>5157A</td>
<td>2.7</td>
<td>O\textsuperscript{2-}</td>
<td>-C-C-</td>
<td></td>
</tr>
<tr>
<td>Annealing after oxidation</td>
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<td>2.7</td>
<td>(OH\textsuperscript{-})</td>
<td>-C-C-</td>
<td></td>
</tr>
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<td>Annealing in vacuum</td>
<td>5157E</td>
<td>2.7</td>
<td>(-C-OH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealing in vacuum</td>
<td>5158E</td>
<td>2.5</td>
<td>O\textsuperscript{2-}</td>
<td>-C-C-</td>
<td>+ Cr\textsubscript{2}O\textsubscript{3} (Fe\textsubscript{x}O\textsubscript{y})</td>
</tr>
<tr>
<td>Annealing in vacuum</td>
<td>5158E</td>
<td>2.5</td>
<td>(OH\textsuperscript{-})</td>
<td>-C-C-</td>
<td>+ Cr Fe-Cr</td>
</tr>
</tbody>
</table>
4.5 Discussion

4.5.1 Behaviour of Fe-Cr Alloy During Oxidation/Reduction

4.5.1.1 Oxidation

As the Fig 4.11.A shows, the intensities of chromium attenuated gradually as more oxygen reached the specimen.

When the cleaned specimen (5156A), which underwent 1 minute etching, was exposed in oxygen to 500L, i.e. exposed at the pressure of 0.5 Torr, for 1000 seconds, (5156E), both the concentration of Fe and Cr decreased (Table 4.13) because of the obvious increase of carbon and oxygen on the surface. The ratio of Fe/Cr, however, increased from 2.50 to 2.93. During the following exposure to 1000L (5156G) and 2000L (5156I) oxygen, the ratio continually increased to 4.68 and 13.74 respectively. It is clear that the surface was becoming richer in iron due to considerable formation of iron oxide during oxidation.

The secondary evidence for the thickening of the iron oxide is the loss of the Fe(0) shoulder on the spectrum, shown in Fig 4.13. The Fe 2p3/2 peak of the cleaned specimen (5156A) presents a shoulder of Fe(0). After the 500L oxygen exposure, this shoulder completely disappeared while Fe(III) satellites are apparent at ~718 eV and ~731.5 eV (BE).

The change of Fe/Cr on the surface and the behaviour of Fe 2p spectra suggest the probable mechanism: During the oxidation of the specimen, the metallic iron, as the major metal (~83%) was oxidised, and an oxide film grows on the surface. At the same time, the chromium, as a minor constituent (~17%) may form an oxide almost immiscible with that of the
iron. The affinity of Cr for oxygen is greater than that of iron, so the chromium in the metallic phase tends to reduce the iron oxide to the lower valence condition. Because the solubility of the oxide of Cr in the Fe oxide is small, cations of Cr rarely pass into the film of oxide of iron. The chromium oxide is likely to accumulate at or near the base of the main film of iron oxide. Therefore the location near the surface becomes impoverished in Cr, the ratio Fe/Cr thus increases. The chromium in this region is present as oxide Cr\textsubscript{2}O\textsubscript{3}.

This process can be schematically shown as Fig 4.15, (A)-(B). The enrichment of iron and the formation of its oxide film on the surface are confirmed by the change of slope of post-peak of both Fe and Cr spectra, which will be discussed in Section 4.5.2.1 in detail.

4.5.1.2 Reduction

On vacuum annealing there is a reversal of the processes occurring during oxidation: the Fe/Cr ratio decreased (Table 4.13) and a steady reduction of the iron oxides to give an increased proportion of metallic and ferrous iron in the spectrum, Fig 4.13, 5157C.

When the specimen, which had been exposed to 2000L oxygen, was heated in vacuum, chromium diffused from the substrate towards the overlayer of iron oxide which was reduced to a lower-valence state. The ratio Fe/Cr decreased from 13.74% to 3.33% after 120 minutes' heating in vacuum, and the Fe(II) satellites appeared at \(-715\) eV and \(-729\) eV (BE) in the iron spectra of 5157(A-G). The reduction process is schematically shown as Fig 4.15, (B)-(C).
Fig. 4.15 Schematic diagram showing the in-depth distribution of Cr and Fe during oxidation and vacuum annealing.
The angular experiments offered some more detailed information about the behaviour of the 515 steel heated in vacuum for 90 minutes without the preceding oxidation treatment.

Two depth profiles were presented in Section 4.4.3. The calculated angular profiles deduced from both models agreed fairly well the experimental angular profile.

Comparing Fig 4.8.B and Fig 4.8.C, it should be noted that two profiles basically are same for depths of < 24 Å. Both have a very thin region being rich in iron (~2 Å) near the surface. Under this layer, the concentration of chromium is higher than that of iron (at depth = 4~8 Å), i.e. there is a region which is rich in chromium. In fact, it is rich in Cr₂O₃, which is formed by the reaction Fe₅O₇ + Cr → Cr₂O₃ + Fe (or Fe(II)) during the heating in vacuum.

The two depth profiles, however, showed an obvious difference with the depth > 24Å. The model shown in Fig 4.8.B implies a sharper interface created from rapid oxidation. The Fig 4.8.C gives another mechanism in which a internal oxidation takes place. It suggests that a rugged interface was brought about. This kind of reaction is usually present at a low oxygen pressure.

By using XPS, information from depths greater than 2λ (~30 Å) cannot be obtained exactly. Therefore, it is difficult to decide which model is the true situation.

But, considering the results of the depth profile (No 5155), even after 6 minutes' etching, the ratio Fe/Cr was 2.39, which is still lower than that of bulk (~5), and no sharp change of ratio Fe/Cr was found during the etching, which suggests that the model in Fig 4.8.C is more likely.

As for the reason that a very thin layer rich in iron remains on the top
after the specimen was heated in vacuum for 90 minutes, the following possibilities should be considered:

(1) The reaction between FeₙOᵥ and Cr is incomplete. It could be confirmed by a long-term heating;

(2) The reduction of iron oxide by chromium goes to chemical completion but the back diffusion of iron is a much slower process and metallic iron is trapped as a surface layer by the impermeable nature of the chromium oxide layer underlying it (221).

(3) Because the Fe ions (and atoms) in the monolayer on the top are at a high vacuum of ~10⁻⁹ Torr, the segregation of the reduced species to the surface may be stable and stronger than that of the atoms or molecules underneath. When the Cr ions located under the top layer try to replace the iron ions in the top layer, they have to overcome so much obstruction that the reduction of oxide of iron can not be finished ultimately.

If (2) and (3) are correct, even when the heating time lengthens, the rich Fe layer still remains on the top.

4.5.2 Energy Loss Background

As mentioned in Section 4.1, further understanding of the energy loss structure of photoelectron peaks enhances the use of data obtained by electron spectroscopy. In this section, it will be shown how the energy loss background can be used to provide extra information on the depth distribution of near-surface elements during the oxidation/reduction of the alloy 515.

4.5.2.1 Post-Peak Slope (P-PS)
For the case of layered structures, when the thickness of the overlayer increases, the photoelectrons emitted from the lower layer have to undergo more inelastic scattering, lose more energy, and appear on the lower kinetic (higher binding) energy side of the peak. Thus the value of P-PS increases.

The Fig 4.14 and Table 4.14 show the P-PS calculated over a range of 25 eV beyond the Cr and Fe peaks during the oxidation of specimen.

It is obvious that the P-PS of the chromium increases with increased exposure of oxygen of the specimen, for which, there are two possible reasons.

The first is the deposition of carbon on the surface formed by the cooling of the exposed specimen to room temperature, as shown by the increase of the height of carbon peaks and atomic percentage of carbon.

The second possible reason is that the oxide of iron formed over the oxide of chromium, as mentioned early in Section 4.5.1.1. The influence of the deposit of carbon on the peaks of iron should be the same as on chromium. In contrast to the P-PS of chromium, however, the P-PS of iron peaks did not increase with exposure, but decreased instead.

Therefore, we have a tendency to think that the great increase of chromium P-PS is principally due to formation of the overlayer of oxide of iron. For the case of iron, even though the deposit of carbon would increase the loss energy of iron peaks because of inelastic scattering and thus increase its P-PS, the concentration of iron on the surface offset this effect, and the P-PS decrease remained unaltered.

4.5.2.2 Base Line Slope
As mentioned in Section 4.4.2 and 4.4.3, it is difficult to get a good fit for those spectra recorded after heating the specimen in vacuum, see Fig 4.7.A and 4.9.A. By changing the base line from a horizontal to a downward inclined line, the better fitting was obtained, Fig 4.7.B and 4.9.B. The Fig 4.7 is used as an example to explain the above fact. In Fig 4.7.A, A and B are two points on the energy loss tail of component Cr(III). Compared with B, A should correspond to those photoelectrons which came from the layer near the surface, and therefore underwent less inelastic scattering and lost less energy. If there were the same concentrations of Cr at different depths, the energy loss tail would appear horizontal, $I_A = I_B$. As mentioned above, however, the concentration of Cr in the region near the surface is higher than that of substrate. So the intensity of photoelectrons coming from the deeper level should be smaller than $I_A$. When the slope of base line was 900 counts/eV, $I_B < I_A$, see Fig 4.7.B, the fitting was better.

For the angular experiments, No 5158, both models suggest a very thin top layer rich in iron. Under this layer, there is a region which is rich in Cr$_2$O$_3$. Further, the concentration of Cr becomes lower again in the bulk of 515 steel.

Fig 4.16 is a simplified schematic diagram which correlates the spectrum of Cr 2p$_{3/2}$ with the layered structure.

For take-off angle $\theta=15^\circ$, the information obtained from superficial level is:

A/O intensity ratio between the tail and peak increased by the layer which is rich in iron;

B/O not or very little influenced by low Cr in bulk metal;
Fig. 4.16 Schematic diagram correlating the energy loss of Cr photoelectrons with the layer structure

Fig. 4.17 Schematic diagram correlating the energy loss of Fe photoelectrons with the layer structure
In this case, there was a smaller slope value.

For $\theta = 60^\circ$, suppose that the photoelectrons traverse the same effective depth, and the spectrum involved the information from the top layers and the low Cr region (alloy bulk),

$A'/O'$ ratio may remain similar as $A/O$;

$B'/O'$ ratio decreases a lot by low Cr concentration in metal.

So, the base line appeared with a larger slope value.

The results of curve fitting show that a good fit could be achieved when slope = 50, for $\theta = 15^\circ$

= 900, for $\theta = 60^\circ$, see Table 4.12.

In this investigation, most iron peaks were fitted over the range of 38 eV (702-740 eV) which is much wider than the fitting range of Cr spectra (~25 eV). Consequently, those photoelectrons which were emitted from iron and passed a longer distance than that in the case of Cr will be involved.

Fig 4.17 schematically presents a Fe 2p$_{3/2}$ peak.

For $\theta = 15^\circ$,

$A/O$ ratio is nearly the same as for pure surface compound;

$B/O$ ratio is lower, because of the low Fe of the region in which Cr$_2$O$_3$ is major compound;

$C/O$ ratio is higher because of the high Fe in the metal phase.

In this case, the base line presents as an upward inclined line and the intensity difference between $B$ and $C$ is relatively distinct, the absolute value of slope should be higher.

For $\theta = 60^\circ$,

$A/O$ is still the same as for the surface compound;
B/O increases because of high iron in the deeper level;
C/O remains high.
As a result, compared with \( \theta = 15^\circ \), the difference between B and C is smaller, i.e. the absolute value of slope is smaller. The Table 4.11B shows,
when slope = -60, for \( \theta = 15^\circ \)
= -20, for \( \theta = 60^\circ \), that good fits have been obtained.

4.5.2.3 ELTH

X-ray photoelectron peaks of elements are always accompanied by the electron energy loss tail on the higher binding energy side of the peak due to the inelastically scattered photoelectrons. To resolve the difficulty which arises for those specimens including two or more chemical states distributed in layer-like fashion by using Shirley background, the background signal of each component was handled separately in the previous work from this laboratory (216, 152). The electron energy loss tail height ELTH can be used to supplement the peak information.

As mentioned in Section 4.4, when the 515 steel, which has a thin layer of oxide of Fe on the surface because of exposure to the atmosphere during and after polishing of the sample, was heated in vacuum, the Cr diffused from the substrate to the superficial layer to reduce the oxide of iron and to reform an overlayer being rich in \( \text{Cr}_2\text{O}_3 \). As the heating period was prolonged, this overlayer became thicker and the distance travelled by photoelectrons emitted from the substrate necessarily increased. These electrons lost more energy while they passed through the overlayer because of the inelastic scatterance. The increase of ELTH of Fe(0) and Fe(II+III)
with the heating shown in Table 4.3 is evidence for the above understanding.

Confirmation of the ELTH as a surface feature was obtained by argon etching. From Table 4.5, the overlayer containing the oxide of Fe and Cr, but rich in Cr₂O₃, which formed during the 90 minutes' vacuum annealing, became thinner and thinner after each etching. Then the ELTH of Fe(0) and Fe(II+III) regularly decreased from 52% for Fe(0) to 36% for 6 minute etching.

37% Fe(II+III) 7%,

In fact, the concentration of the Fe oxide is very small and does not generate its own loss feature after etching a few times. For chromium, however, as shown in Table 4.8 even in the later stages of the depth profile, the ELTH values for Cr(0) and Cr(III) remain at ~60% and ~30% of peak height respectively. This indicates that there is a substantial Cr₂O₃ overlayer on the metallic substrate. This is to be expected from thermodynamics as the partial pressure of oxygen required to form Cr₂O₃ is much less that for formation of Fe₂O₃/Fe₃O₄/FeOOH.

The above values of ELTH of Cr(0) and Cr(III) obtained in 5155 are as expected from a simple substrate overlayer system for thin film on chromium as shown in the previous work of this laboratory (215).

The results obtained by considering the ELTH as a function of take-off angle further confirmed that ELTH may provide a useful method to aid in characterisation of near surface distribution of elements and ions and thus is particularly helpful when ion-etching is undesirable.

Table 4.11A shows that ELTH of Fe(0) and Fe(II+III) varied as the function of take-off angle (i.e. the function of the effective depth by photoelectrons which passed through the oxide overlayer.) For example, the
higher values of ELTH, 61% for Fe(0) and 55% for Fe(II+III), correspond to the longer effective distance for the photoelectrons emitted at $\theta=15^\circ$. Conversely, when $\theta=60^\circ$, the photoelectrons travelled a shorter distance within the overlayer, therefore lost less energy, and the ELTH appeared as the smaller values, 54% for Fe(0) and 38% for Fe(II+III).

Summary

The chemical properties of a solid surface depend not only on the chemical composition of the surface layer, but also on the in-depth distribution of elements in the near surface region. The two conventional techniques, the angular and sputter depth profiling, both involve the recording of several electron spectra and in addition for the latter, sequential ion bombardment of the surface, thus are time-consuming. A further disadvantage of sputter depth profiling is that the sample is destroyed during analysis. Therefore it is expected that the observation of the energy loss structure could be used as an alternative way of obtaining information on depth composition profiles.

As shown above, the energy loss structures, tail height, post-peak slope and background slope, of photoelectron peaks have offered very useful information to aid in the characterisation of the near surface distribution of elements and ions for the study of oxide films.

This information has been used for studying the passive films formed in the air and aqueous solution during the investigation of the pitting corrosion on stainless steel 316, which will be discussed in the next chapter.
Chapter 5

Pitting Corrosion at Inclusions

5.1 Introduction

As already discussed, the useful corrosion resistance of stainless steel depends upon the presence of a protective oxide film. In aqueous environments pitting may occur at gaps or defects in this surface layer, especially at site of inclusions. It is very important, therefore, to know the composition of the surface layer and that of the layer below the surface as well as the behaviour of the inclusions during formation of pits.

As shown in Chapter 2, pitting corrosion has been intensively studied for more than fifty years. The propagation of pits is relatively well understood and is comparatively insensitive to the structure of the metal. On the other hand, pit initiation which is of course the necessary precursor to propagation, is less well understood but is probably far more dependent on metallurgical structure. During the past two decades, a considerable contribution to the advancement on corrosion science has been made by surface analysis, and in particular, by the use of XPS and AES. The study of surface chemistry over a very small area of surface, for example, corrosion pits and inclusions, became possible with the availability of high resolution scanning Auger electron microscopy.

In this investigation the commercial stainless steel, 316, has been used to study the mechanism of pitting. Attention was concentrated on the compositions and properties of the oxide films formed in the air, their...
transformation to the aqueous passive films and the behaviour of inclusions. A combination analysis of XPS, AES and EDX has been utilized. XPS was used to study the surface composition and chemistry of films on the stainless steel. The high resolution scanning Auger electron microscope, in which simultaneous AES and EDX could be performed, was used to investigate the areas with inclusions and pits and to follow the changes before and after exposure to sodium chloride solution.

5.2 Experimental

5.2.1 Material and Specimen Preparation

Type 316 stainless steel has been investigated. The chemical composition of the steel is listed in Table 5.1.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td>0.051</td>
<td>0.27</td>
<td>1.69</td>
<td>0.015</td>
<td>0.009</td>
<td>2.39</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td>17.05</td>
<td>11.14</td>
<td>0.45</td>
<td>&lt;0.03</td>
<td>rest</td>
</tr>
</tbody>
</table>

The specimens of stainless steel 316 were cut with a die from cold rolled sheet 1 mm thick to give circular test samples of 10 mm in diameter.
The samples were ultrasonically cleaned in acetone to remove particles and machine oil which might stick on their surface during production. The samples were wet ground using 240, 400, 600 and 1200 grit silicon carbide papers and followed by polishing with diamond paste to a one micron finish. Then they were degreased in acetone and rinsed thoroughly with pure water before being dried in a stream of cold air and stored in a desiccator. The final repolish was performed with 1 μm alumina on dry cloth to give a clean surface suitable for surface analysis before the specimens were transferred to the instruments. The above preparation procedures were adopted for both ESCA and SAM investigation.

The inclusions on the highly polished surface have poor contrast in the SEM. In order to identify the inclusion area and to trace the changes after exposure in corrosive solution, the sites of inclusions are first marked using a Vickers micro hardness tester to give microhardness indentations visible under the optical microscope. They must be further located within the boundary of the indentations by X-ray mapping. A typical map in sulphur radiation is illustrated in Fig 5.00 (upper left quadrant). At this stage the Auger map (upper right) of the surface composition to a depth of 1 nm, is very indistinct because of contamination from the polishing process. The Beilby layer is therefore removed in stages using the Auger signal to control the ion etching process until the sulphur Auger signal has the same clarity as that of the bulk. The lower quadrants in Fig 5.00 give the Auger maps after the removal of 1 and 6 nm respectively. The colour scale used on Link 860 is shown in Fig 5.01.
Fig 5.00 Sulphur maps illustrating removal of Beilby layer from prepared surface
(a) X-ray map
(b) Indistinct Auger map because of contamination from the polishing process
(c, d) Auger maps after the removal of 1 nm and 6 nm of the Beilby layer respectively by argon ion etching.

Fig 5.01 The colour scale used on Link 860.
5.2.2 Test Environment

3.5% NaCl solution was prepared from analytical grade sodium chloride and ultra-pure water. In the experiments where the pH value of NaCl solution was taken as a variable, a few drops of 1 M hydrochloric acid or 1M sodium hydroxide (analytical reagent) were utilized to bring the solution to a starting pH as required.

All experiments were carried out at room temperature between 22°-26°C.

The polished and marked specimens were transferred to the MA500 where they were cleaned using a argon ion beam (this is more fully discussed in Section 3.3.2 and 5.2.1) in order to remove any modified surface resulting from the polishing process.

After detailed measurement of Auger and X-ray spectra on the sites which appeared to be interesting and after taking maps from the elements considered important, the samples were removed from the microscope and transferred immediately to a dish of sodium chloride solution to prevent re-contamination of the surface. After a given immersion, the samples were briefly washed by immersion in ultra-pure water, dried by blotting with tissue on a lower corner, returned to the microscope and the same area re-examined.
5.2.3 Surface Analysis

5.2.3.1 XPS Study on Passive Film of Stainless Steel 316

To study the surface compositions of the air formed and aqueous passive films of stainless steel 316, all of the specimens were prepared as mentioned in Section 5.2.1. They were then cleaned by etching with the argon ion in the analyser chamber of the ESCA3. MkII, in order to remove some oxide left on the surface after polishing. The air formed passive films were obtained by exposing these cleaned specimens to air for 10 hours after being taken out of the instrument.

The transition from the air formed film to the aqueous film was investigated by immersing the above specimens in 3.5% NaCl neutral solution for the desired lengths of time individually. The specimens were also washed and dried as mentioned above.

Following each treatment, the photoelectron spectra were recorded. To study further the in-depth distribution of elements of the aqueous passive film one specimen, which had been exposed to the 3.5% NaCl solution for 40 minutes, was observed at the take-off angles given in Table 5.2. Also the etch depth profile was obtained from the same specimen.

The experimental procedure together with the test number are shown in Table 5.2.
Table 5.2 The Experimental Procedure and Test Number

<table>
<thead>
<tr>
<th>No of specimen</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>7</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry polished</td>
<td>DP03</td>
<td>DP07</td>
<td>DP11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Etch 2 minutes</td>
<td>DP03E2</td>
<td>DP07E2</td>
<td>DP11E2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exposure to air</td>
<td>A01</td>
<td>A02</td>
<td>A03</td>
<td>A04</td>
<td>A05</td>
<td>A07</td>
<td>A11</td>
</tr>
<tr>
<td>Exposure to 3.5% NaCl solution</td>
<td>NA001</td>
<td>NA003</td>
<td>NA005</td>
<td>NA000</td>
<td>NA010</td>
<td>NA040</td>
<td>NA120</td>
</tr>
<tr>
<td>Exposure time, min</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>0</td>
<td>10</td>
<td>40</td>
<td>120</td>
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</tbody>
</table>

Angular XPS

<table>
<thead>
<tr>
<th>θ</th>
<th>No</th>
<th>Time, sec</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°</td>
<td>N40A15</td>
<td>0</td>
<td>E4000</td>
</tr>
<tr>
<td>25°</td>
<td>N40A25</td>
<td>30</td>
<td>E400300R</td>
</tr>
<tr>
<td>35°</td>
<td>N40A35</td>
<td>60</td>
<td>E40060</td>
</tr>
<tr>
<td>45°</td>
<td>N40A45</td>
<td>90</td>
<td>E40090</td>
</tr>
<tr>
<td>60°</td>
<td>N40A60</td>
<td>120</td>
<td>E40120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>E40180</td>
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<td></td>
<td></td>
<td>270</td>
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<td></td>
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<td>E40360</td>
</tr>
<tr>
<td></td>
<td></td>
<td>480</td>
<td>E40480</td>
</tr>
</tbody>
</table>
5.2.3.2 Auger and X-ray Spectra

An accelerating beam voltage of 15 kV was used throughout since this voltage gives better Auger signals for most experimental conditions and is sufficiently energetic to excite useful X-ray lines from the elements considered.

In most of the cases, the tilt-angle from the primary electron beam was kept at ~45°. A specimen current of 7.5 nA was used for the tungsten filament, while 15 nA was for the LaB₆ filament.

For Auger measurement, the hemispherical analyser is used with 4mm slits and the CRR mode is chosen.

All Auger spectra were acquired under computer control over a range of 1000 eV with a channel width of 1eV for wide scans or a varied range (depending on the element considered) with a channel width of 0.2 eV for narrow scans using the direct acquisition. The counting times for widescans were 300 seconds or 600 seconds.

The X-ray spectra were acquired over the range 0-10 keV with the channel width of 20eV, and a counting time of 100 seconds.

5.2.3.3 Auger and X-ray Mapping

The simultaneous Auger and X-ray mapping acquisition was utilised. Thus, maps showing both surface (AES) and bulk (EDX) compositional features could be obtained from a given region of the sample, during a single experiment.

The software for the product DIGIMAP is made up of two separate suites of programs: these are the products ADM and DIGIPAD.
ADM (Acquire Digital Maps) is a program which can be used primarily for the acquisition of digital images, and not for viewing or processing them; that is done using the DIGIPAD (Digital Image Processing And Display).

In the case of Link 860, up to 4 energy windows may be defined for Auger mapping, allowing 4 elements to be mapped in the same experiment. If the background maps were needed, only 2 elements could be mapped at a time. X-ray data from up to 8 additional windows could be recorded simultaneously.

In the case of Link AN10000, the total number of digital sources and EDX windows selected cannot exceed 32 in Disk Acquisition mode, or 12 in RT (Real-Time) mode. Individually, no more than 24 EDX windows may be selected at any one time.

The required dwell time can be gauged from the count rates observed while using the analyser. The dwell time of 50 milliseconds for per pixel was used to give enough intensity for every element during acquisition in this work. The resolution of images, which means the number of pixels in either the vertical or horizontal dimension of an image, was 128*128.
5.3 Results and Discussion

5.3.1 Surface Composition of Passive Films of SS316

5.3.1.1 Air Formed Passive Film

As mentioned in Section 5.2.3.1, in order to study the surface composition of air formed passive film, all specimens were polished and argon etched for 2 minutes and then followed by the exposure to the air. Among them, three specimens have been analysed after the polishing and argon ion etching. The surface compositions are shown respectively in Table 5.3 and 5.4. To exclude the effect of carbon and simplify discussion, the composition of the surface was normalized for O, Cr, and Fe. These results are shown in these Tables beside the unnormalised element concentrations.

<table>
<thead>
<tr>
<th>Table 5.3 Surface Compositions of Dry Polished Specimens</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>Fe/Cr</td>
</tr>
</tbody>
</table>
Table 5.4 Surface Compositions of Argon Etched Specimens

<table>
<thead>
<tr>
<th>No Atom%</th>
<th>DP03E2</th>
<th>DP07E2</th>
<th>DP11E2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With C</td>
<td>Without C</td>
<td>With C</td>
</tr>
<tr>
<td>C</td>
<td>27.9</td>
<td>27.7</td>
<td>26.2</td>
</tr>
<tr>
<td>O</td>
<td>44.3</td>
<td>61.4</td>
<td>39.7</td>
</tr>
<tr>
<td>Cr</td>
<td>8.7</td>
<td>12.1</td>
<td>8.9</td>
</tr>
<tr>
<td>Fe</td>
<td>19.1</td>
<td>26.5</td>
<td>23.7</td>
</tr>
<tr>
<td>Fe/Cr</td>
<td>2.20</td>
<td>2.66</td>
<td>2.16</td>
</tr>
</tbody>
</table>

Although a great effort was made to keep conditions constant for each sample during both polishing and argon ion etching, the surface compositions obtained from these specimens still showed some variation. This could impute an importance to the position of the sample in the batch processed together. The specimens may have had differing retention period in the air after they were polished or in the instrument vacuum before the spectra were recorded. For instance, the specimen No. 11, had been exposed to the atmosphere about 2 hours longer than the specimen No. 03, because it had been polished earlier. Thus the oxygen concentration of DP11R was higher than that of DP03, see the data normalized to Cr, Fe, and O, in Table 5.3. Also this is confirmed by the broader width of the oxygen peak of DP11R-2, compared with the oxygen peak of DP03-2, Fig 5.1. While the photoelectron spectra were recorded for No. 11 specimen, there was a failure of the computer, and the analysis had to be repeated. Probably, as a result, the carbon concentration of DP11R was higher than that of DP03, as can be seen from Table 5.3 and from the intensities of the carbon peaks.
Fig 5.1  The broadening of oxygen peak by a further 2 hours retention period in the air after the dry polishing
Fig 5.2 The survey spectra showing an increased P-PS of Fe peak due to the increased carbon contamination
Fig 5.3 Various tail heights on Fe 2p spectra caused by different retention periods in the air after the dry polishing
on the survey spectra. Fig 5.2. It is the energy loss background which
confirms that the carbon is surface contamination. Comparing the narrow
in DR11R;
scan spectrum of Fe with that of DP03, Fig 5.3, it is found that DP11R had
a higher tail, because the Fe photoelectrons emitted from the material
under the contamination layer lost kinetic energy and appeared on the
higher binding energy side, the effect being greater the thicker the layer.

Comparing the compositions of surface measured before and after argon
etching for each individual specimen, it is evident that the carbon and
oxygen concentration on the surface decreased after argon ion etching,
owing to the removal of carbon contamination and some oxide of Fe and Cr
from the specimen surface, see Table 5.3 and 5.4. These tables also show
the concentration of both Fe and Cr increased obviously during the argon
etching.

Furthermore, all argon etched specimens were taken out of the ESCA3
MkII, and exposed to the air for 10 hours, then transferred into the
instrument again, followed by recording XPS spectra. The surface
compositions of the air exposure specimens are shown in Table 5.5.

When these specimens had been exposed into the air, the oxidation of
iron and chromium took place. The concentration of Fe and Cr on the
surface reduced, which was compatible with the increase of oxygen, and
indicated the formation of new air-formed passive films, Table 5.4 and 5.5.

The Fe/Cr ratios on the surface for three parallel specimens are listed
in Table 5.6, with the experimental conditions together. Despite the fact
that there was some difference among these samples, the Fe/Cr ratios of
three specimens were increased by the argon ion etching, and decreased by
the air exposure without any exception. This means that the chromium
enrichment appeared in both dry polished surface and newly air-formed
<table>
<thead>
<tr>
<th>No</th>
<th>Atom%</th>
<th>A01 (+C)</th>
<th>A02 (+C)</th>
<th>A03 (+C)</th>
<th>A04 (+C)</th>
<th>A01 (-C)</th>
<th>A02 (-C)</th>
<th>A03 (-C)</th>
<th>A04 (-C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>31.0</td>
<td>28.7</td>
<td>33.3</td>
<td>34.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>46.8</td>
<td>67.8</td>
<td>50.6</td>
<td>68.5</td>
<td>41.0</td>
<td>62.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>7.2</td>
<td>10.4</td>
<td>6.9</td>
<td>9.7</td>
<td>7.0</td>
<td>10.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>13.4</td>
<td>19.4</td>
<td>12.3</td>
<td>17.3</td>
<td>14.5</td>
<td>22.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>1.3</td>
<td>1.9</td>
<td>1.2</td>
<td>1.7</td>
<td>2.4</td>
<td>3.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.36</td>
<td>0.52</td>
<td>0.37</td>
<td>0.52</td>
<td>0.43</td>
<td>0.66</td>
<td></td>
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</tbody>
</table>

Fe/Cr 1.86 1.78 1.72 2.07

<table>
<thead>
<tr>
<th>No</th>
<th>Atom%</th>
<th>A05 (+C)</th>
<th>A07 (+C)</th>
<th>A11 (+C)</th>
<th>A05 (-C)</th>
<th>A07 (-C)</th>
<th>A11 (-C)</th>
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<tr>
<td>C</td>
<td>32.1</td>
<td>37.6</td>
<td>35.5</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>44.4</td>
<td>65.4</td>
<td>42.5</td>
<td>51.2</td>
<td>79.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>6.1</td>
<td>9.0</td>
<td>5.3</td>
<td>8.5</td>
<td>4.2</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>15.0</td>
<td>22.1</td>
<td>12.8</td>
<td>20.5</td>
<td>7.8</td>
<td>12.1</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>1.9</td>
<td>2.8</td>
<td>1.4</td>
<td>2.2</td>
<td>1.1</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.52</td>
<td>0.77</td>
<td>0.30</td>
<td>0.48</td>
<td>0.21</td>
<td>0.33</td>
<td></td>
</tr>
</tbody>
</table>

Fe/Cr 2.50 2.42 1.86

If the compositions are normalized for O, Cr and Fe, the mean concentrations of the seven air exposure specimens are:

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>Cr</th>
<th>Fe</th>
<th>Fe/Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg</td>
<td>69.3</td>
<td>10.07</td>
<td>20.61</td>
<td>2.04</td>
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</tbody>
</table>
Table 5.6  The Ratio of Fe/Cr on the Surfaces

<table>
<thead>
<tr>
<th>No</th>
<th>3</th>
<th>7</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry polished</td>
<td>2.14</td>
<td>2.25</td>
<td>1.76</td>
</tr>
<tr>
<td>Etched 2 min</td>
<td>2.20</td>
<td>2.66</td>
<td>2.16</td>
</tr>
<tr>
<td>Exposure to air</td>
<td>1.72</td>
<td>2.42</td>
<td>1.86</td>
</tr>
</tbody>
</table>

passive film compared with a fresh argon etched surface, because of the higher affinity of chromium for oxygen.

The concentration of Fe, Cr and O were plotted with the treatments in Fig 5.4, as the left part.
Fig. 5.4 Concentrations of O, Fe, Cr on the surfaces under various treatments.
5.3.1.2 The Transition from the Air Formed to Aqueous Passive Films

To trace the change from an air formed film to an aqueous film, a set of experiments was carried out, in which the air exposed specimens were immersed individually in 3.5% NaCl solution (pH ~7) for various period of time, then photoelectron spectra were taken from each sample. The results associated with those recorded from un-immersed specimen were collected in Table 5.7.

It is shown that the contents of the Ni and Mo on the surfaces of both air and aqueous oxide films are low compared with those of the bulk stainless steel 316, which is consistent with the results of Hashimoto (14), Lumsden (12), and Cahoon (13) et al.

Chlorine was not detected until the specimen was exposed to chloride solution for 40 minutes.

Again, the surface compositions of these specimens were normalized for Cr, Fe, and O. They were listed in Table 5.7, and plotted with the exposure times in Fig 5.4, as the right part.

It is shown that the most important changes in the nature of the surface layer on the stainless steel 316 were observed during the first 10 minutes' exposure, especially in the first 5 minutes. Once the specimen had been immersed in the solution, the concentration of oxygen on the surface increased massively due to the increase of adsorbed and bound water, which was also confirmed by the increase of the width of oxygen peaks on the high binding energy side. The FWHM of oxygen peak was ~3.5 eV for the air formed films, but 4.0, 4.1, 4.3 eV for the aqueous films formed with 1, 3, 10 minutes exposure respectively. Therefore, the relative
Table 5.7 Surface Compositions of Aqueous Passive Films (Formed in 3.5% NaCl Solution)

<table>
<thead>
<tr>
<th>No</th>
<th>Atom%</th>
<th>NAO00 (+C)</th>
<th>NAO00 (-C)</th>
<th>NAO01 (+C)</th>
<th>NAO01 (-C)</th>
<th>NAO03 (+C)</th>
<th>NAO03 (-C)</th>
<th>NAO05 (+C)</th>
<th>NAO05 (-C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>39.6</td>
<td>45.4</td>
<td>45.1</td>
<td>45.7</td>
<td></td>
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<tr>
<td>O</td>
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<td>65.7</td>
<td>38.9</td>
<td>71.2</td>
<td>41.9</td>
<td>76.3</td>
<td>40.0</td>
<td>73.7</td>
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</tr>
<tr>
<td>Cr</td>
<td>6.4</td>
<td>10.6</td>
<td>5.1</td>
<td>9.3</td>
<td>4.6</td>
<td>8.4</td>
<td>5.1</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>12.5</td>
<td>20.7</td>
<td>9.4</td>
<td>17.2</td>
<td>7.4</td>
<td>13.5</td>
<td>8.2</td>
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</tr>
<tr>
<td>Ni</td>
<td>1.5</td>
<td>2.5</td>
<td>0.84</td>
<td>1.5</td>
<td>0.85</td>
<td>1.5</td>
<td>0.70</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.22</td>
<td>0.36</td>
<td>0.29</td>
<td>0.53</td>
<td>0.22</td>
<td>0.40</td>
<td>0.28</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>Fe/Cr</td>
<td>1.95</td>
<td>1.84</td>
<td>1.61</td>
<td>1.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No</th>
<th>Atom%</th>
<th>NAO10</th>
<th>NAO40</th>
<th>NAO120</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>51.1</td>
<td>46.8</td>
<td>57.4</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>37.5</td>
<td>69.1</td>
<td>40.2</td>
<td>75.6</td>
</tr>
<tr>
<td>Cr</td>
<td>4.1</td>
<td>7.6</td>
<td>4.4</td>
<td>8.3</td>
</tr>
<tr>
<td>Fe</td>
<td>6.6</td>
<td>12.2</td>
<td>7.1</td>
<td>13.3</td>
</tr>
<tr>
<td>Ni</td>
<td>0.43</td>
<td>0.79</td>
<td>0.97</td>
<td>1.8</td>
</tr>
<tr>
<td>Mo</td>
<td>0.26</td>
<td>0.48</td>
<td>0.22</td>
<td>0.41</td>
</tr>
<tr>
<td>Cl</td>
<td>0.41</td>
<td>0.77</td>
<td>0.20</td>
<td>0.47</td>
</tr>
<tr>
<td>Fe/Cr</td>
<td>1.61</td>
<td>1.61</td>
<td>1.51</td>
<td></td>
</tr>
</tbody>
</table>

The concentration of iron and chromium on the surface reduced rapidly. The loss of material from the surface by selective dissolution continuously continued.
modified the composition of the passive layer over the period of time.

Considering the variation of the surface composition induced by the
small differences during the processing and staying of samples, the ratio
of the surface concentration between unexposed and exposed (to solution)
specimens, $R_E$, is used for Cr, Fe, and O to give the relative changes of
these constituents during the exposure. The values of $R_E$ are shown in
Table 5.8 and Fig 5.5.

Similarly, an apparent ratio between $R_{E, Cr}/R_{E, Fe}$, called as
$R_{E, Cr}/R_{E, Fe}$, is used. The values of $R_{E, Cr}/R_{E, Fe}$ were also plotted as a function
of exposure time in Table 5.8 and Fig 5.5. It is interesting to notice
that the increase of the apparent ratio $R_{E, Cr}/R_{E, Fe}$ is not obscured by the
relative decrease of ratio $R_{E, Cr}$ within the first 3 minutes, which is
due to the obvious influence of adsorbed and bound water.

After the high-speed transition from air to aqueous film (take about 10
minutes), the rate of composition change on the surface gradually slowed
down, and the $R_{E, O}$ and $R_{E, Cr}/R_{E, Fe}$ no longer increased. This indicated that
the new aqueous film had formed and the surface became passivated by a
film, in which the concentrations of Fe and Cr are less than those in air-
formed passive film. The film is richer in chromium than iron, shown by
the increase of $R_{E, Cr}/R_{E, Fe}$ as the formation of the aqueous films proceeds,
see the right column of Table 5.8. This enrichment of chromium in the
passive films formed on austenitic and ferritic stainless steel have
already been reported by many workers (12-15). The measurement in this
work is consistent with previous studies. Later work in this laboratory
shows that the enrichment of chromium in the surface layers is caused by
the selective dissolution of iron as the film is formed, which agreed with
analysis of the solution in which the surface was passivated (222).
Table 5.8  \( R_{E, O}, R_{E, Cr}, R_{E, Fe} \) and Apparent Ratio \( R_{E, Cr/Fe} \)

<table>
<thead>
<tr>
<th>No</th>
<th>Exposure Time</th>
<th>0</th>
<th>Cr</th>
<th>Fe</th>
<th>( R_{E, Cr/Fe} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA000</td>
<td>0</td>
<td>0.98</td>
<td>1.02</td>
<td>1.07</td>
<td>0.95</td>
</tr>
<tr>
<td>NA001</td>
<td>1</td>
<td>1.00</td>
<td>0.97</td>
<td>1.00</td>
<td>0.97</td>
</tr>
<tr>
<td>NA003</td>
<td>3</td>
<td>1.11</td>
<td>0.77</td>
<td>0.72</td>
<td>1.07</td>
</tr>
<tr>
<td>NA005</td>
<td>5</td>
<td>1.14</td>
<td>0.85</td>
<td>0.66</td>
<td>1.29</td>
</tr>
<tr>
<td>NA010</td>
<td>10</td>
<td>1.15</td>
<td>0.91</td>
<td>0.60</td>
<td>1.52</td>
</tr>
<tr>
<td>NA040</td>
<td>40</td>
<td>1.11</td>
<td>0.97</td>
<td>0.65</td>
<td>1.49</td>
</tr>
<tr>
<td>NA120</td>
<td>120</td>
<td>1.12</td>
<td>0.88</td>
<td>0.65</td>
<td>1.35</td>
</tr>
</tbody>
</table>
Fig. 5.5 Variation of $R_E$ as a function of exposure time in 3.5% NaCl solution, pH=7.

$R_E \times 10^{-1}$

- $\Delta = Cr/Fe$
- $\circ = 0$
- $\times = Cr$
- $\Box = Fe$

Exposure time (minutes)
5.3.1.3 In-depth Distribution of Elements in Aqueous Films on SS316

5.3.1.3.A Angular Experiments

To study further the in-depth distribution of elements of the aqueous film the specimen, which had been exposed to 3.5% NaCl solution for 40 minutes, was analysed at take-off angles of 15°, 25°, 35°, 45° and 60°. The compositions obtained and the results normalized to O, Cr, Fe, Ni and Mo as well as the ratio of Fe/Cr are listed in Table 5.9.

Excluding the effect of carbon contamination, the oxygen concentration decreases regularly with the variation of emission angle, from 15° to 60°. The width of oxygen peak (FWHM) became broader as the angle was lower. Table 5.10 shows the widths of oxygen peaks as a function of the take-off angle. Careful observation of the oxygen spectra indicated that the broadening took place mostly on the high binding energy side, which means that the proportions of OH⁻ and H₂O in the whole envelope of oxygen peak was larger when the spectra were taken from the top region, where the oxygen was present partly as bound water.

It is quite clear that there exists a minimum in the ratios of Fe/Cr as the take-off angle changed from 15°-60°. The ratio Fe/Cr was 2.24 when the 15° of take-off angle was used. As the take-off angle increased to 25° and 35°, the Fe/Cr decreased to 1.92 and 1.88 respectively. When take-off angle further increased to 45° and 60°, however, this ratio increased in reverse to 1.96 and 2.02.

As discussed in Section 3.4.1, the basic principle of angular XPS is the increase in surface sensitivity obtained at low angles of electron exit to the surface. A layer-like distribution in the aqueous passive film,
Table 5.9  Angular Profile for the Aqueous Film

<table>
<thead>
<tr>
<th>No</th>
<th>(^{\circ})</th>
<th>C</th>
<th>O</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Fe/Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>N40A15, 15'</td>
<td></td>
<td>74.3</td>
<td>19.6</td>
<td>1.7</td>
<td>3.8</td>
<td>0.53</td>
<td>0.10</td>
<td>2.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>76.3</td>
<td>6.6</td>
<td>14.8</td>
<td>2.1</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N40A25, 25'</td>
<td></td>
<td>67.4</td>
<td>24.3</td>
<td>2.6</td>
<td>5.0</td>
<td>0.51</td>
<td>0.13</td>
<td>1.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>74.5</td>
<td>8.1</td>
<td>15.4</td>
<td>1.6</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N40A35, 35'</td>
<td></td>
<td>57.2</td>
<td>29.8</td>
<td>4.1</td>
<td>7.7</td>
<td>0.64</td>
<td>0.50</td>
<td>1.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>69.8</td>
<td>9.6</td>
<td>18.0</td>
<td>1.5</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N40A45, 45'</td>
<td></td>
<td>55.1</td>
<td>30.1</td>
<td>4.6</td>
<td>9.0</td>
<td>0.95</td>
<td>0.26</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>67.1</td>
<td>10.1</td>
<td>20.1</td>
<td>2.1</td>
<td>0.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N40A60, 60'</td>
<td></td>
<td>47.3</td>
<td>33.9</td>
<td>5.5</td>
<td>11.1</td>
<td>1.6</td>
<td>0.55</td>
<td>2.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>64.3</td>
<td>10.5</td>
<td>21.1</td>
<td>3.1</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.10  FWHM of Oxygen Peaks as A Function of Take-off Angle

<table>
<thead>
<tr>
<th>No</th>
<th>Take-off angle</th>
<th>FWHM, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>N40A15</td>
<td>15'</td>
<td>4.2</td>
</tr>
<tr>
<td>N40A25</td>
<td>25'</td>
<td>4.0</td>
</tr>
<tr>
<td>N40A35</td>
<td>35'</td>
<td>3.7</td>
</tr>
<tr>
<td>N40A45</td>
<td>45'</td>
<td>3.4</td>
</tr>
<tr>
<td>N40A60</td>
<td>60'</td>
<td>3.3</td>
</tr>
</tbody>
</table>
The outer region was enriched in carbon and high BE oxygen. Sugimoto et al. (20) suggested that oxygen in the film is present in two different binding states: M-O type bond and M-OH or M-O-OH type bonds. The high BE part in the envelope of oxygen peak should correspond to the latter. Under this layer, there was a very thin oxide layer which is relatively enriched in iron. The inner region differed in Fe/Cr ratio and the oxide contained more chromium, which is responsible for the minimum on the ratio Fe/Cr. Underneath this Cr rich oxide layer, the composition corresponded to the bulk of stainless steel. So, a minimum value in the ratio of Fe/Cr presented at 35° of the take-off angle.

As already shown in Chapter 3 and 4, when the iron photoelectrons emitted from the deeper level travel to the surface, they will lose some kinetic energy and form an electron energy loss tail. The relative height of this tail compared with its major peak should increase with the increasing effective depth traversed by the iron photoelectrons. If photoelectrons pass through the same overlay at various take-off angle, the larger angle will correspond a shorter effective depth.

To normalize the tail height of Fe 2p peaks (at BE = 736 eV) for the peak height of Fe 2p_{3/2} (at BE = ~ 710 eV), the intensity ratios between $I_{736\text{eV}}$ and $I_{710\text{eV}}$ were obtained. As a function of the take-off angle these ratios are shown as following:

<table>
<thead>
<tr>
<th>Take-off angle $\theta$</th>
<th>15°</th>
<th>25°</th>
<th>35°</th>
<th>45°</th>
<th>60°</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{736\text{eV}}/I_{710\text{eV}}$</td>
<td>1.39</td>
<td>1.29</td>
<td>1.20</td>
<td>1.15</td>
<td>1.06</td>
</tr>
</tbody>
</table>
It is found that the relative height of tail decreased regularly as the larger angle was used, because a shorter path has to be traversed by the iron photoelectrons in the chromium rich overlayer.

5.3.1.3.B In-depth profile from argon etching experiments

After the angular experiments, the same specimen (exposed to 3.5% NaCl solution for 40 minutes) was bombarded with argon ion beam followed by recording the XPS spectra on the residual surface left after a certain sputtering time.

The surface compositions are shown in Table 5.11 as the function of etch time. Again, the compositions were normalized for O, Cr, Fe, Ni and Mo excluding C and Ar. The results and the ratio of Fe/Cr are also listed in Table 5.11.

It is shown that the first 2 etchings of 30 seconds greatly decreased the concentration of oxygen of the surface, from 74.1% → 59.1% → 51.9%. At the same time, the FWHM of oxygen peak changed from 3.7 eV to 3.0 eV, and the decrease of the peak width took place on the high BE side. This indicates that the bound water exists in the top layer and is consistent with the results obtained from the angular work.

The ratios of Fe/Cr were shown in Fig 5.6 as a function of the etch time. As the removal of the upper passive film by argon ion etching, the ratio of Fe/Cr increased regularly from 1.71 (before etching) to 3.34 (the total sputtering time was 360 seconds). This also implied the presence of the chromium rich layer.
<table>
<thead>
<tr>
<th>No</th>
<th>Time. sec.</th>
<th>C</th>
<th>O</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Ar</th>
<th>Fe/Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>E4000</td>
<td>0</td>
<td>61.9</td>
<td>28.2</td>
<td>3.5</td>
<td>6.0</td>
<td>0.24</td>
<td>0.15</td>
<td></td>
<td>1.71</td>
</tr>
<tr>
<td>E40030R</td>
<td>30</td>
<td>35.9</td>
<td>37.4</td>
<td>8.4</td>
<td>14.5</td>
<td>2.8</td>
<td>0.28</td>
<td>0.74</td>
<td>1.73</td>
</tr>
<tr>
<td>E40060</td>
<td>60</td>
<td>28.6</td>
<td>36.5</td>
<td>9.4</td>
<td>20.2</td>
<td>4.0</td>
<td>0.40</td>
<td>1.0</td>
<td>2.15</td>
</tr>
<tr>
<td>E40090</td>
<td>90</td>
<td>28.2</td>
<td>34.4</td>
<td>8.7</td>
<td>22.5</td>
<td>4.7</td>
<td>0.48</td>
<td>1.2</td>
<td>2.59</td>
</tr>
<tr>
<td>E40120</td>
<td>120</td>
<td>27.7</td>
<td>34.0</td>
<td>8.0</td>
<td>24.1</td>
<td>4.4</td>
<td>0.45</td>
<td>1.2</td>
<td>3.01</td>
</tr>
<tr>
<td>E40180</td>
<td>180</td>
<td>29.2</td>
<td>31.1</td>
<td>8.1</td>
<td>25.4</td>
<td>4.1</td>
<td>0.63</td>
<td>1.3</td>
<td>3.14</td>
</tr>
<tr>
<td>E40270</td>
<td>270</td>
<td>28.3</td>
<td>29.5</td>
<td>8.5</td>
<td>27.7</td>
<td>4.1</td>
<td>0.69</td>
<td>1.2</td>
<td>3.26</td>
</tr>
<tr>
<td>E40360</td>
<td>360</td>
<td>29.6</td>
<td>27.0</td>
<td>8.6</td>
<td>28.7</td>
<td>4.1</td>
<td>0.65</td>
<td>1.3</td>
<td>3.34</td>
</tr>
<tr>
<td>E40480</td>
<td>480</td>
<td>30.3</td>
<td>25.7</td>
<td>8.8</td>
<td>29.2</td>
<td>4.0</td>
<td>0.68</td>
<td>1.3</td>
<td>3.32</td>
</tr>
</tbody>
</table>
Fig. 5.6 Fe/Cr ratios plotted as a function of the argon etch time for the specimen exposed in 3.5% NaCl solution for 40 minutes.
When the specimen was further etched for another 120 seconds, the surface composition showed only very slight change. The narrow scan spectrum of Fe showed a typical metallic iron peak, see E40480.4 in Fig 5.7. These facts indicated that the sputtering reached the bulk stainless steel.

Further evidence of the layer-like fashion of this film was given in Fig 5.8. The Figure shows a steady decrease in slope associated with the iron peak as carbon contamination and chromium rich layer were removed during the argon etching.

The peaks of iron recorded before and after 1 minute and 8 minutes etching are shown in Fig 5.7. The intensity of peak tail shows an obvious decrease with the increase of the sputtering time (i.e thickness of etched overlayer) when compared with the intensities of their major 2p_{3/2} peaks. This figure also shows the difference in the shape of the Fe spectra between unetched aqueous film and etched surfaces. The centre of gravity of the iron peak was moved to the lower BE side as the overlayer was taken away during sputtering, which illustrates the various chemical state of iron at the different depth of the passive film.

The sputtering condition in this work gave the etching rate of ~6.2 Å/min (in Ta2O5 scale), thus the thickness of the passive film formed at 40 minutes' exposure could be considered to be about 30Å.
Fig 5.7 The iron 2p spectra recorded before and after argon etching, showing the in-depth distribution of different Fe compounds, and the decreased tail height with the increased sputtering time.
Fig. 5.8 The survey spectra showing a steady decrease in slope associated with the iron peaks as carbon contamination and the Cr rich layer were removed during the argon etching.
From the work discussed in this section the following conclusions were drawn: When the cleaned 316 specimens are exposed to the air, the oxidation of iron and chromium takes place, and the concentration of oxygen of the surface increases. In the air-formed passive film, the ratio of Fe/Cr is lower than that of a fully argon etched surface, which means that chromium enriches on the surface during the formation of the film.

When an air-exposed sample is immersed in the 3.5% NaCl solution, the transition from an air-formed film to an aqueous film rapidly changes the composition of the surface in the first 10 minutes. After the 10 minutes, this film became passivated. In the aqueous passive film, the chromium enriches further compared with the air-formed film due to the selective dissolution of iron. The concentration of oxygen in this film is higher than that of the air-formed passive film.

The results obtained from the angle resolved XPS and the argon ion etch profile indicate that the aqueous passive film formed by the 40 minutes' exposure has a layer-like fashion structure. The thickness of this film is about 30 Å.

The above XPS study gave an understanding on the surface composition for both air- and aqueous-formed passive films. When these passive films break down on the site of inclusions during the exposure of specimens to the corrosive solution, pits may initiate on such area. The mechanism of the initiation of pitting will be discussed in the following sections.
5.3.2 Inclusions of Stainless Steel 316 (SS316)

The study described here focuses attention on the inclusions and their types, and also on the behaviour of these inclusions under the influence of different aqueous solution containing Cl⁻ ions.

The observation of a number of inclusions shows that there exist two types of inclusions in the SS316. The first one consists of separate sulphide particles, and the other is composed of sulphides occurring as a complex with oxide inclusions.

A typical example of the separate manganese sulphide inclusions is shown in Fig 5.9, which is a secondary electron image of this group of inclusions.

The EDX spectra (Fig 5.10) measured from these inclusions indicates the enrichment of sulphur and manganese compared with those recorded from the matrix of stainless steel (Fig 5.11). The X-ray maps of sulphur and manganese showed their enrichment in the sites of inclusions (Fig 5.12), and the maps of iron and chromium on the same area show the impoverishment of these elements, see Fig 5.12.

As a surface sensitive technique, AES measurement in the same area shows the Auger peak of sulphur is relatively weak because of the contamination resulting from the sample preparation procedure. The AES signal and maps were used to assist in the removal of such polishing films in order that the corrosion exposure gave rise to an unimpeded attack in the vicinity of the inclusion. As the contamination was removed, the peaks of sulphur and manganese became more intense and distinct maps were
Fig 5.9 SEI of the separate sulphide inclusion group
Fig 5.10  EDX spectrum measured from the sulphide inclusion shown in Fig 5.9

15 kV, 7.5nA, Live time 100s, Channel width 20eV
Fig 5.11 EDX and AES spectra recorded from the matrix of stainless steel

15 kV, 7.5 nA

EDX: Live time 100s; Channel width 20 eV

AES: CRR 2; Scans 5; Total 600 seconds
Fig 5.12  X-ray maps of the inclusion group shown in Fig 5.9
obtained. Fig 5.13 shows this effect. The Auger spectra a and b were measured respectively for the polished surface and the argon ion etched surface after 10 minutes' etching. Both were recorded from the centre of the lower inclusion. As mentioned in Section 5.2.1, Fig 5.00 also shows sulphur X-ray and Auger electron maps illustrating removal of the Beilby layer from the prepared surface. The Auger maps of sulphur, manganese and iron taken after the removal of ~6 nm (10 minutes etching) are shown in Fig 5.14. The etching, however, did not make any obvious difference for X-ray spectra and maps which relate to the bulk composition.

As discussed in Section 5.3.1, the surface compositions obtained from the individual samples showed some variation despite the effort which was made to keep the condition constant during the preparation of these specimens. Therefore, it is also expected that the cleaned surface (by the argon etching) may give a more constant surface condition on each specimen for the followed exposure experiment, and make it easier to compare the results obtained from the various solutions.

Fig 5.15. shows the secondary electron image of another inclusion group which is a typical example of sulphides occurring together with oxides in a single inclusion.

The Auger and X-ray analyses have been done for numbers of points on different positions of this inclusion group, and the Auger and X-ray maps were recorded for varied elements on the cleaned surface and shown in Fig 5.16 (Auger maps of Fe, S, Cr) and Fig 5.17 (X-ray maps of Fe, S, Cr, Mn, Ni, Ti, Al).
Fig 5.13  AES spectra obtained from the inclusion group shown in Fig 5.9
15 kV; 7.5 nA; CRR 2; Scans 5; Total 300 seconds

a. For the polished surface
b. For the argon ion etched (10 minutes) surface
Fig 5.14 The Auger maps taken after the 10 minute etching
a. Fe;   b. S;   c. Mn
Fig 5.15  SEI of the inclusion group of the mixture of sulphide and oxide particles
Fig 5.16 Auger maps of Fe, S, and Cr on the cleaned surface
Fig. 5.1/ X-ray maps on the cleaned surface

Fe

Cr
Fig 5.17  X-ray maps on the cleaned surface
Fig 5.17 X-ray maps on the cleaned surface
Fig 5.17  X-ray maps on the cleaned surface
These analyses and maps indicate the following facts:

(1) In all areas where there are inclusions iron and nickel have low concentrations compared with the matrix of stainless steel. Auger and X-ray maps show the overall shape of the inclusion group by the reduction in the iron signal.

(2) Among these inclusions, some particles, such as those on the top and bottom, possess a similar composition to the first kind of inclusions mentioned above, i.e. they exist as manganese sulphide. Both spectra and maps show the rich sulphur and manganese, and the poor iron, nickel and chromium.

(3) Another category of particles, such as the middle one, is different from the first kind. The maps show that they possess rich concentrations of Cr, Ti, Al as well as Mn in the major part of this particle, and some manganese sulphide present at the edge of the particle. Fig 5.18 is the X-ray spectrum recorded from the middle particle.

The shape of the oxygen peak on the Auger spectrum (Fig 5.19), which is different from those recorded on cleaned MnS inclusions (Fig 5.13b) and steel matrix (Fig 5.11), implied that it is present as the oxide of these elements.

(4) It seems that the Mn is present in both the sulphide and the oxide inclusion.

(5) This inclusion group is shown to be a mixture of sulphide and oxide particles.

Sulphur is soluble in molten steel, but its solubility in the solid phase is very low. It is precipitated in the form of metal sulphide during solidification of the steel, and the precipitation pattern is influenced by
Fig 5.18 The X-ray spectrum recorded from the centre of the oxide particle (Top)

Fig 5.19 The Auger spectrum recorded from the centre of the oxide particle (Bottom)
its strong segregation tendency. The precipitation of sulphide from the sulphur-rich liquid phase is facilitated by existing nuclei, which are usually the oxides. Oxide inclusions with an outer rim of sulphide are therefore common in commercial stainless steel.

As showed in Section 2.4, in many prior works, particular attention was paid to the influence of sulphide and oxide inclusions on pitting of Fe-Cr and Fe-Cr-Ni alloys and stainless steels. The view is generally expressed that the most susceptible sites for pit nucleation in those materials are the Mn, Fe sulphide. However, there are some suggestions in the literature that all nonmetallic inclusions are able to provoke the pit nucleation.

In the present work, the Auger electron and X-ray examinations revealed that all sulphide inclusions in the stainless steel 316 are rich in Mn, but not rich in Fe, whether they are in the separate sulphide or in the mixture of sulphide and oxide inclusions. The role played by these non-metallic inclusions in the nucleation of pitting in this stainless steel is determined by the detailed analysis of these inclusions and their behaviour on exposure to sodium solutions at various pH values.
5.3.3 Surface Chemistry on the site of inclusions

It is known that on a polished steel, sulphide inclusions act as initiation sites for localized corrosion, but the process through which this phenomenon occurs remains to be properly resolved. During the last twenty years, most observations were made by scanning electron microscopy with EDX or microprobe analyses. In order to understand the mechanism of pit initiation, surface-sensitive information about the distribution of elements on the site of inclusions and the surrounding region is still required. A study which traces the progress of the pit initiation as a function of the exposure time will be helpful for this understanding.

5.3.3.1 Initiation of Pits in 3.5% NaCl Solution

The specimen, on which the measurement and mapping have already been done, was repeatedly exposed to 3.5% NaCl solution for the required time periods, then returned to the microscope and followed by re-examination of the same area. The exposures of 35, 45, 30, 40 and 300 minutes were given progressively. Thus the accumulative exposure times were 35, 80, 110, 150 and 450 minute respectively.

5.3.3.1.A Secondary Electron Images

A series of scanning electron micrographs of the inclusion group shown in Fig 5.15 is presented in Fig 5.20 (a, b, c, d). It shows the change of topography at the site of inclusions with the exposure period.

It is clear that a pit formed at the site of inclusions, and corrosive
Fig 5.20 The SEI series of the inclusion group shown in Fig 5.15, which shows the change of topography at the site of inclusions with the exposure.
attack on manganese sulphides was more severe. The pit was getting deeper and deeper due to the dissolution of MnS and metal as the exposing time lengthened, whilst attack on the oxide surface could not be observed with any degree of confidence.

5.3.3.1.B X-ray and Auger Spectra

After every exposure, X-ray and Auger spectra were recorded at a number of points on the inclusions and surrounding area. The Fig 5.21 shows those measured points.

By correlating the ratio between the peak heights of sulphur and iron Kα lines of X-ray spectra with the exposed time, the corrosion progress could be followed, see Table 5.12.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td></td>
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</tr>
<tr>
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<td></td>
</tr>
<tr>
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<tr>
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<td>-10</td>
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</tr>
<tr>
<td>-5</td>
<td>9.67</td>
</tr>
</tbody>
</table>

The ratios of H_s/H_Fe,K decreases regularly with the exposure time, which agrees with the secondary electron images, and confirms semi-
quantitatively the dissolution of MnS.

For Auger spectra, after 35 minutes exposure, only relatively weak sulphur peaks were observed on the MnS inclusions, Fig 5.22, P7 (on the top particle), nor was sulphur found at surrounding areas of the inclusions. See, e.g., Fig 5.22, P55, which was recorded from the area adjacent to the bottom MnS particle.

When the specimen was exposed for 450 minutes, however, the sulphur peak intensities dramatically increased on the surface of sulphides, (P10, Fig 5.23), which is recorded from the point 10 on bottom particle. Sulphur was observed also on the surface of an oxide inclusion (P3, Fig 5.23) as well as on the area surrounding the inclusions (P53, Fig 5.23). The similar measurements were taken on points 51, 52, 54, and the results confirmed each other. Also the Auger spectra from points 61, 62, 63, 64 were recorded, Fig 5.24. The distances from the right edge of inclusion (point 61) to point 62, 63, 64 are W/2, W and 2W respectively, here 'W' represents the width of inclusion at horizontal direction. It was found that the sulphur signal got weaker with the increased distance, and no sulphur peak was seen on point 64. This evidence suggested that sulphide ions are released by corrosive attack on sulphides in the crevice at the periphery of the oxide inclusion and MnS particles and they spread to the whole surface of the inclusion group and near surroundings.

The Auger spectra revealed moreover that chloride accumulation was accompanied by sodium accumulation. Since the Na⁺ and Cl⁻ ions can come only from the corrosive solution, it seems probable that traces of the corrosive solution either remained on the surface of the micropit and its vicinity, or were trapped in the FeCl₂ layer formed there, Fig 5.23. However, in the early stage of the exposure, the Auger spectra did not show
Fig. 5.21 Measured points on the inclusion group of the mixture of MnS and oxide, and on the area surrounding the inclusions.
Fig 5.22 Auger spectra from the MnS particle and surrounding area after 35 minutes of exposure to 3.5% NaCl solution (pH = 7)
Fig 5.23 Auger spectra from the surface of MnS, oxide, and surrounding area after 450 minutes of exposure to 3.5% NaCl solution (pH = 7)
Fig 5.24 Auger spectra recorded from the surface beside the inclusion group and with a distance of 2W, after 450 minute exposure.
Fig 5.25 Auger spectrum recorded from the white spot in the top particle shown in Fig 5.20, after 450 minute exposure.
the accumulation of Na⁺, although the Cl peaks were obvious.

Some attention was paid to the possibility that an accumulation of chloride might arise at the seemingly uniform metal surface, apart from any inclusion. It was found possible to detect the deposit of chloride on the metal surface using high contrast in the second electron image. It seems, however, that in the absence of non-metallic inclusions the accumulations of sodium chloride do not nucleate pits, since pronounced corrosion attack has generally been found at the inclusions.

It is interesting to see the spectrum recorded from the white spot of the top particle in Fig 5.20, P7', which was left unattacked by the corrosive solution within the site of an inclusion. It presents a strong sulphur peak and Cu peak and seems to be copper sulphide. Fig 5.25. This supports the observation made by Daud (134). In his work, copper enriched-MnS inclusions showed no sign of micro-crevice formation and the surface became smooth and apparently inhibited.

5.3.3.1.C X-ray and Auger Maps

After 35 minutes immersion, X-ray maps of the specimen were taken for elements Al, S, Ti, Cr, Mn, Fe, and Ni, and Auger maps for elements Fe, S and Cl.

By using DIGIMAP programme, a three-element map of Fe (red), Cr (yellow) and S (blue) has been obtained from individual maps of these elements, Fig 5.26 b, while the maps of Fe, S, Cr were shown in Fig 5.27. Similarly, the three-element map for original inclusion group (before the exposure) is shown in Fig 5.26 a.

Comparing Fig 5.26 a and b, the sulphide was dissolved by attack on
Fig 5.26 The behaviour of the mixture inclusion group during 35 min of exposure in 3.5% NaCl solution (pH = 7)
Fig. 5.2b The behaviour of the mixture inclusion group during 35 minutes of exposure in 3.5% NaCl solution (pH = 7)

a. X-ray three-element (Fe, S, Cr) map before exposure

b. X-ray three-element (Fe, S, Cr) map after 35 minutes of exposure

c. The Auger maps of Fe, S, and Cl after 35 minutes of exposure
Fig 5.27  The X-ray maps obtained after 35 minutes of exposure
Fig 5.27 The X-ray maps obtained after 35 minutes of exposure
sulphides in the crevice at the periphery of the chromium (and Ti, Al, Mn) oxide inclusion, and further diffused to its vicinity at this early stage of corrosive attack. After the 35 minutes of exposure, therefore, the sharp boundary between the oxide and the sulphide, which was presented on the Fig 5.26a, became obscure (light blue). This is shown on the Fig 5.26b. This is also confirmed by the comparison of the S maps in Fig 5.17 and Fig 5.27. The signal contrast of the X-ray sulphur map decreased during the exposure by the dissolution of sulphide, especially at the periphery of the multielement oxide. By comparing the Mn maps of the mixed sulphide/oxide inclusions, before and after the exposure, (Fig 5.17 and Fig 5.27), it is found that the intensity of manganese at the sulphide sites decreased because of the dissolution of MnS inclusions, whilst, by contrast, the intensity of manganese at the site of the oxide became stronger.

Fig 5.26c shows Auger maps of Fe, S, and Cl respectively illustrating that chloride ions cluster at the surface of the oxide and the sulphides inclusions. In this stage the aggregation of the chloride ions on the sulphides is even less severe. However, it seems that the rich chloride ions on the oxide surface did not cause more severe attack.

When the specimen was exposed in the solution for long period, for example, of 450 minutes, the X-ray maps show that the iron and nickel signal at the bottom particle (on MnS inclusion) already approached the intensity level of the surrounding steel matrix, Fig 5.28, and the sulphur signal had greatly weakened compared with those shown in Fig 5.17 and Fig 5.27. By contrast, the chromium, titanium and aluminum maps (Fig 5.28) showed their oxides have not been corroded very much by the corrosive solution and maintained high signal intensities. It is noticeable that the manganese intensity of particles at the top and bottom almost decreased
Fig 5.28 The X-ray maps obtained after 450 minutes of exposure
Fig 5.28  The X-ray maps obtained after 450 minutes of exposure
Fig 5.28 The X-ray maps obtained after 450 minutes of exposure
Fig 5.28 The X-ray maps obtained after 450 minutes of exposure

Fe, Cr;
S, Mn;
Ni, Ti;
Al
to the same level as the metallic matrix adjacent to the inclusions, but that in the middle particle did not decrease, Fig 5.28. It can be seen (Fig 5.17, 5.27, 5.28) from the distribution of S, Cr and Mn that Mn bound with S is removed from the inclusions, whereas both the Mn and Cr (Al, Ti) bound with oxygen remain almost intact within the pit. The above results indicate that in stainless steel, the corrosion pits are preferentially nucleated at the sulphide inclusions. The oxide inclusions do not cause nucleation of pits. These support the suggestion given by Z. Szklarska-Smialowska et al (227, 136). They studied the effect of sulphide inclusions on the nucleation of pits in a commercial 18Cr-9Ni austenitic stainless steel at a constant potential of 0.5 V in a 0.5N NaCl solution. Their electron microprobe observations showed corrosion pits initiated at mixed manganese and iron sulphide inclusions, present either in the form of separate particles, or as shells surrounding the oxides. No pitting occurred at particles composed only of oxides. However, in one of their first works on the formation of pits on single crystals of high purity 16% Cr-Fe alloy, the authors using the microprobe technique, found that the pits nucleate predominantly at inclusions of chromium oxide (135).

Auger maps (Fig 5.29) for 450 minutes' exposure show the distribution of iron, sulphur and chloride. In this stage, sulphur spread to a wider range, and the chloride ions clustered on MnS have stronger intensity, which is confirmed by the Auger spectra. The Cl map would suggest that the Cl\textsuperscript{-} accumulation occurs at the MnS inclusions, especially at the boundary of the sulphide inclusion. The drop in the iron signal became indistinct because of the spread sulphur.

These results support the observation of Szummer et al (137) on electron microprobe study of Cl\textsuperscript{-} agglomeration at sulphide inclusions in
Fig 5.29 The Auger maps obtained after 450 minutes of exposure
Fig 5.29 The Auger maps obtained after 450 minutes of exposure

+ a. Fe;
+ b. S;
+ c. Cl
iron and stainless steel. In their investigation, the samples of 18Cr-9Ni stainless steel were polarised at $E = -200 \text{ mV}_{\text{SCE}}$, and at $E = -10 \text{ mV}_{\text{SCE}}$, both of which potentials are more negative than the corresponding $E_{\text{NP}}$, (potential of pit nucleation) in the borate buffer solution containing 0.5M KCl. Electron microprobe analysis of these samples revealed some spots on the metal surface where Cl$^{-}$ accumulation took place. These spots were mainly localized at the boundaries between metal matrix and non-metallic inclusions. Some chloride accumulation had also been detected at discrete points on a seemingly uniform metal surface, but the areas of these points were much smaller and the corresponding intensities of Cl were generally lower than those found at inclusion/matrix boundaries. Their microprobe analysis of the areas of chloride accumulation occurring at the boundaries of non-metallic inclusions revealed that the Cl$^{-}$ accumulation was accompanied by some K$^{+}$-accumulation.

In the experiments of Szummer et al (137), at the end of the polarisation the anode was transferred into the benzene layer above the aqueous corrosive solution to provide quick dehydration of the specimen surface and prevent the possible dissolution of the nuclei of the chloride salt layer formed at discrete points on the surface. However, in the present work, after a given exposure, the specimen were briefly washed by immersion in ultra-pure water to stop the reaction. This procedure also prevents the deposit of salt on the surface from the solution, which can be considerable. It is noticed that Cl peak does not appear on the X-ray spectra recorded from the exposed specimen, but did on those Auger spectra. This suggests that Cl$^{-}$ clustered on the surface of the inclusions and the vicinity, but the concentration was too low to detect for the X-ray analysis which gives the bulk information. As a surface sensitive
technique, the Auger analyses provided the distribution of elements and ions during the exposure and showed that AES is a powerful tool for understanding the mechanism of the initiation of pits.

5.3.3.2 The Effects of pH Value

In an aqueous environment, metallic corrosion proceeds via an electrochemical mechanism. Vermilyea (223) assumed that at a critical potential (i.e., the pitting potential), the protective metal oxide, the salt of the metal, and the aggressive anions are in equilibrium. When a metal reacts with water, it may either form soluble cations or form directly a passive film. Clearly, the reaction that occurs is important since the first will result in corrosion while the second will result in less, possibly very much less, corrosion, depending upon the properties of the film.

The thermodynamic data on reactions between many metals and water have been measured, collected, and calculated by Pourbaix (224). They have been combined with solubility data on oxides and hydroxides and with equilibrium constants for reactions of these to produce Pourbaix diagrams which indicate thermodynamically stable phases as a function of electrode potential and pH. Although they convey no information on rates of reaction, these diagrams provide a strong thermodynamic basis for understanding corrosion reactions. Numerous workers in the field of corrosion have used potential-pH diagrams in order to throw more light on the mechanism of a corrosion process. As discussed in Section 2.3, the pH of the solution has differing effects on the pitting potential for various metals. In order to further understand the effect of pH on the initiation of pits formed on the stainless steel 316, experiments were carried out in
solutions of sodium chloride at pH values of 5 and 9 respectively. The results will be compared with that obtained from experiments in neutral NaCl solution.

The conditions for Auger spectroscopy in this work were slightly different: a LaB$_6$ filament was used on the MA500 to obtain higher brightness. A beam current of 15 nA was used in the following Auger and EDX analyses, although the spatial resolution remains approximately the same as before.

5.3.3.2 A pH value of 5

Hydrochloric acid was used to bring the NaCl solution to a starting pH value of 5. As stated in Section 5.3.3.1, the specimen was repeatedly exposed in the solution for the required times, and total exposures of 15, 35 and 80 minutes were made. Auger and X-ray measurements were taken from two groups of inclusion: the separate MnS (M33 group) and the mixture of MnS and multi-element oxide (M34 group).

Fig 5.30 shows the M34 group of the mixed inclusions, on which EDX and Auger point analyses have been taken from several points. As before (5.3.3.1.B), the ratio between the peak heights of sulphur and iron K$_\alpha$ lines of the X-ray spectra was used to follow the dissolution of the MnS inclusions. These ratios are listed in Table 5.13 as a function of the exposure time. The same analyses were carried out for an inclusion group of separate MnS particles shown in Fig 5.31 and the ratios are shown in the same table.
Fig 5.30 The picture of the M34 mixture inclusion group showing the points of measurements

Fig 5.31 The picture of the M33 separate MnS inclusion group showing the points of measurements
Table 5.13 \( R_{\text{ts}}/R_{\text{rm}} \) of X-ray spectra as a function of the exposure time (pH = 5)

<table>
<thead>
<tr>
<th>No</th>
<th>Exposure time (minutes)</th>
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<th>15</th>
<th>35</th>
<th>80</th>
</tr>
</thead>
<tbody>
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<td>M34 -1</td>
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<td>3.8</td>
<td>1.0</td>
<td>1.0</td>
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</tr>
<tr>
<td>-2</td>
<td>6.4</td>
<td>2.4</td>
<td>1.9</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>-4</td>
<td>13.5</td>
<td>5.9</td>
<td>2.5</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>M33 -1</td>
<td>10.1</td>
<td>4.5</td>
<td>3.2</td>
<td>1.4</td>
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<tr>
<td>-2</td>
<td>4.5</td>
<td>4.3</td>
<td>1.3</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>-3</td>
<td>25.0</td>
<td>10.7</td>
<td>3.0</td>
<td>3.3</td>
<td></td>
</tr>
</tbody>
</table>

* M34 - MnS and multi-element oxide
M33 - MnS

For the M34 group, the X-ray point analyses and maps showed that the top and bottom particles are MnS, while the centre part of the middle particle is oxide of Cr, Ti, Al as well as Mn and the periphery of the oxide is MnS. The X-ray maps of Fe, S, Mn and Cr are shown in Fig 5.32, and those of Al, Ni and Ti are in Fig 5.33. A new colour scale, Fig 5.34, is made to suite both secondary electron image and element map. In fact, the left part of this scale is a grey scale aimed to make the secondary electron image look as normal. In order to compare semi-quantitatively the intensities on the maps obtained from various time of exposure, an effort has been made to keep the average brightness constant on the surface of substrate steel for each element respectively.

After the specimen was exposed to the solution for 15 minutes, which is shorter than the first exposure in the case of pH=7 (35 minutes), the X-ray maps, Fig 5.35, showed that the contrast of Fe signal between the inclusion and matrix became weaker; the S and Mn intensities showed obvious reduction compared with those of the original. Also the Cr map did not show any
Fig 5.32 The X-ray maps of M34 group before exposure

Fig 5.33 The X-ray maps of Ni, Ti, and Al for M34 group before exposure
obvious change, which means the multielement oxide did not dissolve. After the further 25 and another 45 minutes' exposure, the intensities of both Mn and S continued to decay as the dissolution of MnS inclusions took place. This is shown in Fig 5.36.

As the exposure progressed, the edge between the inclusion and the matrix of steel became indistinct, which is caused by the dissolution of MnS and the iron metal adjoining the inclusion. Because a more aggressive solution was used, the above process was much more rapid compared with the situation seen in pH=7.

Auger maps showing the surface composition are collected in Fig 5.37: the upper left quadrant is the secondary electron image of M34 inclusion.
group taken before the specimen was exposed to solution. The Fe Auger map (left bottom) shows the overall shape of the inclusion group, which agrees with the SEI. On the top surface of the multi-element oxide, the oxygen map (right top) shows the enrichment of oxygen on the surface of oxide inclusions. The distribution of sulphur is identical with that of X-ray S map shown in Fig 5.32.

The exposure of 15 minutes made a bright ring around the inclusion on the Auger S map, see Fig 5.38. This arose out of the sulphur released from MnS and spread to the area surrounding the inclusion. It was also noticeable that the sulphur Auger signal did not show a higher intensity on the surface of inclusions, even on the top of MnS. The Fe map shows iron is slightly enriched on the surface of the inclusion group, especially on the top of MnS inclusions.

The next exposure of 20 minutes lead to further change: the sulphur ring has a even higher contrast, shown in Fig 5.39. It is very clear that the inclusion group is surrounded by a dark ring on the Fe Auger map, whilst the enrichment of Fe is more apparent on the surface of MnS inclusions, and the surface of the oxide has the lowest intensity of Fe Auger signal.

However, when a further exposure of 45 minutes was carried out (the total exposure time was 80 minutes), the contrast between the inclusion surface and the near surrounding area on the S and Fe maps decreased, as shown in the bottom right quadrant of Fig 5.40. This series of maps shows how the surface condition changed regularly during the exposures to solution.

There are two possibilities which can be considered for this decrease of contrast:
Fig 6.35  The X-ray maps of M34 group after 15 minutes of exposure

3.5% NaCl solution, pH = 5
Fig 5.36  The X-ray maps of M34 group showing the dissolution of MnS and the pit initiation during exposure

3.5% NaCl solution, pH = 5

a. Before exposure;   b. 15 minutes of exposure;
c. 35 minutes of exposure;   d. 80 minutes of exposure.
Fig 5.37 SEI and Auger maps of M34 inclusion group before exposure.

Fig 5.38 SEI and Auger maps of M34 inclusion group after 15 minutes of exposure to the 3.5% NaCl solution, pH = 5.
Fig 5.39 SEI and Auger maps of M34 inclusion group after 35 minutes of exposure to the 3.5% NaCl solution, pH = 5
Fig 5.40  Seis and Auger maps of M34 inclusion group showing the change of element distribution on the surface during exposure in 3.5% NaCl solution, pH = 5

a. Before exposure;  
b. 15 minutes of exposure;  
c. 35 minutes of exposure;  
d. 80 minutes of exposure
Fig 5.4: SEIs and Auger maps for after 80 minutes of exposure as well as for the following 2 minutes of etching.
(1) As the dissolution of MnS is almost finished, no more sulphur can be released from the inclusion, and also the sulphur continued to spread to the over a greater area so that the gradient of sulphur concentration decreased; or,

(2) The mapping took long time, (a few hours); the surface had been covered by carbon contamination; and the real surface distribution was concealed by this contamination.

In order to reveal the reason for above phenomena and to answer what kind of new Fe compounds formed on the top of the inclusion group when the MnS dissolved and the pit initiated, the specimen was etched by argon ions for 2 minutes to remove the top overlayer, after the 80 minutes' exposure and the mapping. Then mapping for Fe, S and O was carried out again. These maps are shown in the bottom right quadrant of Fig 5.41, together with those taken after 60 minute exposure. After the removal of the overlayer, the S map still shows quite weak contrast. Oxygen was rich on the oxide and whole inclusion group surface compared with the surface of surrounding steel. Unfortunately, the etching may have been too severe, so that the Fe signal drop, which corresponded to the site of inclusion group, appeared again.

The results obtained from the separate MnS confirmed above results. The maps from M33 inclusion group are shown in Fig 5.42, 43, 44:

Fig 5.42 shows Auger maps of Fe, S and X-ray maps of Mn, S before the exposure;

Fig 5.43 shows the intensity change on the Auger maps of Fe, S and X-ray maps of Mn and S to follow the dissolution of inclusions and the initiation of pit during exposure;

Fig 5.44 shows the Auger maps of Fe, S, Cl and O, which were taken
Fig 5.42  Auger (Fe, S) and X-ray (Mn, S) maps of M33 inclusion group before exposure

a. AE Fe;  b. AE S;

c. XR Mn;  d. XR S
Fig 5.43 Auger and X-ray maps of M33 inclusion group showing the dissolution of MnS and the pit initiation during exposure

a. Before exposure;     b. 15 minutes of exposure;
c. 35 minutes of exposure; d. 80 minutes of exposure, then argon etch 2 minutes
Fig 5.44 Auger maps of M33 inclusion group

After 80 minutes of exposure to 3.5% NaCl solution, pH = 5, taking mapping then followed by 2 minutes' argon etching

a. Fe; b. S;
c. Cl; d. O
after the specimen underwent 80 minutes of exposure, mapping, and argon ion etching for 2 minutes to remove the contamination. The O map confirmed the enrichment of oxygen on the top surface of MnS inclusions.

5.3.3.2.B pH value of 9

Sodium hydroxide solution was utilised to bring the NaCl solution to a starting pH = 9.

Again, the specimen was repeatedly exposed in the solution. The total exposure of 35, 80 and 450 minutes were given progressively.

The Table 5.14 shows the ratios between the peak heights of sulphur and iron K\textsubscript{s} lines of X-ray spectra as a function of the exposure time for two inclusion groups:

S4 is a mixture of MnS and multi-element oxide;

S3 is a separated MnS inclusion group.

<table>
<thead>
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<th>Table 5.14</th>
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<tbody>
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<td></td>
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</table>
Fig 5.45 The pictures of S4 and S3 inclusion groups showing the points of measurements
a. S4 group;  b. S3 group
Fig 5.46 The X-ray (Fe, S, Cr, Mn) maps of S4 inclusion group during exposure in 3.5 % NaCl solution, pH = 9

a. Before exposure; b. 35 minutes of exposure;
c. 80 minutes of exposure; d. 450 minutes of exposure.
Fig 5.47  The X-ray (Ni, Ti, Al) maps of S4 inclusion group during exposure in 3.5% NaCl solution, pH = 9
a. Before exposure;   b. 35 minutes of exposure;
c. 80 minutes of exposure;   d. 450 minutes of exposure.
The Fig 5.45 shows the positions where the point analyses have been taken.

The X-ray maps of Fe, S, Cr, Mn and Al, Ni, Ti for the inclusion group S4 were taken before and after the required exposure time. These maps are shown in Fig 5.46 and 5.47 respectively.

In the case of pH=9, the X-ray maps showed a good agreement with the results obtained from the point analyses. Although in the early stage of exposure, the behaviour of MnS was similar to the situation of pH=7, and the dissolution of the inclusions was obvious, this process did not continue into the latter stages. The addition of OH\(^-\) appeared to inhibit the corrosion reactions. It is evident that only little change could be seen when the exposure time increased from 35 minutes to 80 minutes, and no visible contrast change was found from 80 to 450 minute exposure.

The Fig 5.48 shows the Auger maps of O, Fe, and S with the secondary electron images as needed to follow the surface change during the exposure.

The oxygen Auger map recorded before the immersion of the specimen shows that the highlight on the map rose from the multi-element oxide surface, the intensity of oxygen on the passive film of the steel is higher than that on MnS inclusion surface, but lower than that from oxide.

The intensity of S on Auger map was obviously reduced when the specimen underwent its first 35 minute exposure. The further exposure, however, did not give distinct changes on the Auger maps of S, Fe and O.

Compared with those taken in the case of pH = 5 and 7, the dissolution of MnS inclusions is much slower and no clear ring of distributed S can be found, even in the latter stage of exposure when the corrosive solution is less severe.

The observation on the inclusion group of separate MnS, S3, provided
Fig 5.46  SEIs and Auger maps of S4 inclusion group

3.5% NaCl solution, pH = 9

a. Before exposure;  b. 35 minutes of exposure;
c. 80 minutes of exposure;  d. 450 minutes of exposure.
Fig 5.49  SEIs and Auger maps of S3 inclusion group

3.5% NaCl solution, pH = 9

a. Before exposure;  b. 35 minutes of exposure;
c. 80 minutes of exposure;  d. 450 minutes of exposure
further the evidence for the different behaviour caused by the various pH values. Fig 5.49 shows the Auger maps of O, Fe and S together with the SEIs for each stage.

The study of Z. Szklarska-Smialowska et al (227) showed that if the sulphide inclusions occurred as separate particles, i.e., without oxides, they were dissolved but did not nucleate pits. The author suggested that the most probable reason for this behaviour seems to be that the geometry of holes produced by the dissolution of sulphide was unfavourable for pit formation, the holes being insufficiently narrow and deep. However, this does not seem to be the case in the present investigation since the two types of inclusion do not show the obviously different behaviour during the exposure.

It is noticed that the Cl Auger maps recorded for pH = 5 and 9 did not show the obvious contrast, which differed from those taken for the case of pH = 7. The probable reason is that a higher beam current (15 nA) was employed in the observation of pH = 5 and 9 with the LaB₆ filament, while 7.5 nA had been used for the measurement of pH = 7. When 15 nA was used, during the acquisition of the Auger spectra, it was found that Cl Auger signal had been seen slightly in the first scan, disappeared in the latter scans. (Usually five scans were taken to build up an Auger spectrum.) The stronger irradiation of electron beam caused the desorption of chloride ions from the surface, thus weakened the Cl signal. When the Auger maps were taken, the dwell time of 50 milliseconds for per pixel was used to give enough intensity for every element during acquisition. However, the chloride ions were removed from the specimen surface and entered the vacuum of the instrument within the dwell of electron beam.
5.3.3.3 The mechanism of initiation of pits on the site of inclusions

The introduction of modern experimental methods, particularly that of the Auger electron microscopy with high spatial resolution, led to interesting conclusions concerning the effect of the composition and distribution of nonmetallic inclusions at the surface of stainless steel on the propensity to pitting. It is, however, worth mentioning that the effect of sulphide inclusions as privileged sites for an intensive local attack was known long ago.

In the 1930s', Tronstad and Sæjested (226) studied carbon steel and found that in 2N NaCl solution the sulphide inclusions initiate the anodic attack on the metal immediately around them, and stimulate localized corrosion. They demonstrated that certain sulphide inclusions, designated as active, are more effective than others, termed inactive, in initiating corrosion attack. The results of the work suggest the active centres consist of the sulphides of iron and manganese. Wranglen (130) also drew attention to differences in the effect of active and inactive sulphides on localized attack. According to Wranglen, the active sulphides are surrounded by extremely fine MnS precipitates, thus making the matrix in their vicinity particularly reactive. The sulphur-segregated matrix close to the sulphide inclusion develops preferential sites that are anodic with respect to the inclusion; whereas, the sulphur-free matrix is cathodic. The active sulphide also act as cathodic sites. The high anode activity in the sulphur contaminated matrix close to active sulphides is ascribed to the large area of contact between a finely divided MnS precipitate and the iron. This means that sulphide ions are close at hand for catalysis of both the anode process, iron dissolution, and the cathode process, which in
the active area seems to consist mainly of hydrogen evolution. The author also has emphasized that the small sulphide particles have a higher solubility than large particles and, furthermore, that anodic areas, as a result of hydrolysis of metal ions, tend to become acidic, facilitating dissolution of sulphides with the formation of \(H_2S\) and \(HS^-\) ions.

Wranglen (130) also suggested a model for the initiation of pitting of stainless steel as shown in Fig 2.10. As the first stage, preferential adsorption of chloride ions occurs on the sulphide inclusions due to its higher electron conductivity, giving stronger electrostatic image forces than on the surrounding oxide film. This was shown by means of a radiochemical method (131). In the present work, Auger spectra shown in Fig 5.22, 5.23 and Cl Auger maps in Fig 5.26 and 5.29 support their suggestion. The measurements showed that chloride accumulation occurs at the surface of inclusions, especially at the boundary of the sulphide inclusions.

The sulphide inclusions exposed on the surface of the stainless steel are not coated with the passive film. Without the protection of this passivating oxide film, the inclusions are directly exposed to the corrosive chloride solution, in which specimens are immersed. The local disturbances in the oxide layer at inhomogeneities of inclusion make these areas more accessible to adsorption of the chloride ions, because the composition in these microareas is different from the rest of the surface. Thus a potential difference can exist which then is amplified by preferential adsorption of the anions. Chloride ions cluster at the surface of the inclusion group, see Fig 5.26.c and 5.29; giving an opportunity to study the above mechanism by use of the surface information from the site of the inclusions and the surrounding region.
Wranglen (130) suggested that the sulphide inclusions are usually less noble than the surrounding passive surface and therefore selectively dissolved and act as small local anodes. In the model shown in Fig 2.10 (130), the author suggested that MnS is primarily oxidised to elementary sulphur according to the electrode reaction:

\[ \text{MnS} = \text{S} + \text{Mn}^{2+} + 2e^- \quad e^0 = -0.10V \text{ for } (\text{Mn}^{2+}) = 1 \]
\[ e^0 = -0.19V \text{ for } (\text{Mn}^{2+}) = 10^{-9} \]
\[ e^0 = -0.27V \text{ for } (\text{Mn}^{2+}) = 10^{-6} \]

Here, the calculated standard potential \( e^0 \) is based on the value of -209kJ/mole for the free energy of formation of MnS.

The observations in the present work support that the corrosive attack starts in the sulphide inclusions proper. The X-ray and Auger analyses showed the dissolution of MnS and the spread of sulphur, which has been discussed in the Section 5.3.3.

However, it seems unlikely from our investigation that this spread of sulphur to the areas surrounding inclusions could be the result of a surface diffusion mechanism associated with elemental sulphur.

Eklund (132) made equilibrium calculations for some sulphide systems actually found in commercial stainless steel. Fig 5.50 shows the potential-pH diagram for the system MnS-H₂O-Cl⁻ calculated on basis of 0.1 mole/litre for SO₄²⁻, Cl⁻, and Mn²⁺, respectively. The numbers and symbols in this potential-pH diagram of the system MnS-H₂O-Cl⁻ refer to the reactions listed in Table 5.15.

From Fig 5.50 it is seen that MnS can exist between pH 4.8 and 13.8 (lines 6 and 8). At pH values less than 4.8, MnS dissolves forming H₂S, Mn²⁺, and MnCl⁺. At pH values higher than 13.8, MnS dissolves forming S²⁻, Mn(OH)₂, and HMnO₄⁻. Line 7, at pH 10.2, corresponds to the formation of
Fig 5.50 Potential-pH diagram for the system MnS-H₂O-Cl⁻ calculated on basis of 0.1 mole/litre for SO₄²⁻, Cl⁻, and Mn²⁺ respectively (After Eklund (132))
Table 5.15 Reaction formula in the potential-pH diagram of the system MnS-H2O-Cl-

a \[ \text{H}_2 = 2\text{H}^+ + 2\text{e}^- \]
b \[ 2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \]
1 \[ \text{S} + 4\text{H}_2\text{O} = \text{SO}_4^{2-} + 8\text{H}^+ + 6\text{e}^- \]
2 \[ \text{H}_2\text{S} = \text{S} + 2\text{H}^+ + 2\text{e}^- \]
3 \[ \text{MnS} = \text{Mn}^{2+} + \text{S} + 2\text{e}^- \]
4 \[ \text{MnS} + 4\text{H}_2\text{O} = \text{Mn}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e}^- \]
5 \[ \text{MnS} + 6\text{H}_2\text{O} = \text{Mn(OH)}_2 + \text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^- \]
6 \[ \text{MnS} + 2\text{H}^+ = \text{Mn}^{2+} + \text{H}_2\text{S} \]
7 \[ \text{Mn}^{2+} + 2\text{H}_2\text{O} = \text{Mn(OH)}_2 + 2\text{H}^- \]
8 \[ \text{MnS} = \text{Mn}^{2+} + \text{S}^2^- \]
9 \[ \text{Mn}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{MnO}_2 + 2\text{H}^+ + 2\text{e}^- \]
10 \[ 2\text{Mn}_3\text{O}_4 + \text{H}_2\text{O} = 3\text{Mn}_2\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \]
11 \[ 3\text{Mn(OH)}_2 = \text{Mn}_2\text{O}_3 + 2\text{H}_2\text{O} + 2\text{H}^+ + 2\text{e}^- \]
12 \[ \text{Mn}^{3+} + 2\text{H}_2\text{O} = \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \]
13 \[ 2\text{Mn}^{3+} + 3\text{H}_2\text{O} = \text{Mn}_2\text{O}_3 + 6\text{H}^+ + 2\text{e}^- \]
14 \[ 3\text{Mn}^{2+} + 4\text{H}_2\text{O} = \text{Mn}_2\text{O}_4 + 8\text{H}^+ + 2\text{e}^- \]
15 \[ \text{HSO}_4^- = \text{SO}_4^{2-} + \text{H}^+ \]
16 \[ \text{HS}^- + 4\text{H}_2\text{O} = \text{SO}_4^{2-} + 9\text{H}^+ + 8\text{e}^- \]
17 \[ \text{H}_2\text{S} = \text{HS}^- + \text{H}^+ \]
18 \[ \text{Fe}^{2+} + 2\text{H}_2\text{O} = \text{Fe(OH)}_2 + 2\text{H}^+ \]
19 \[ \text{Fe}^{2+} + 3\text{H}_2\text{O} = \text{Fe(OH)}_3 + 3\text{H}^+ + \text{e}^- \]
20 \[ \text{Fe}^{2+} + 2.7\text{H}_2\text{O} + 0.3\text{Cl}^- = \text{Fe(OH)}_3\cdot_2\text{Cl}_\alpha\cdot_\gamma + 2.7\text{H}^+ + \text{e}^- \]
Due to the increase in solubility of MnS when the pH is raised, the domain of MnS at higher potentials is limited by the formation of Mn(OH)$_2$ and SO$_4^{2-}$ (line 5). At still higher potentials, MnS dissolves without forming any solid substance (line 4). The highest potential at which MnS can exist is about -100 mV, SHE, (line 3). The dissolution at this potential takes place with the formation of sulphur.

According to Eklund, the sulphides cannot thermodynamically exist at the potential of the passive steel and tend to dissolve. The exposed surface of the inclusions is small compared with the surface of the passive steel. When a specimen is immersed in a solution the potential against the solution is rather noble. As the inclusions are electronic conductors to some extent they will be polarized towards the potential of the steel surface. Thus the sulphides are polarized to a potential at which they will dissolve.

In order to know the potential of stainless steel 316 when immersed in the 3.5% sodium chloride solution, the corrosion potentials were measured as a function of exposure time at pH values 7 and 5, which is shown in Fig 5.51. For pH = 7, the result showed that the potential varied from 128 mV to -49 mV (SCE). The stable values obtained from the measurements are in the range of 0-50 mV (SCE). That is the range of ~ 240-290 mV in the SHE scale. In the case of pH 5, the measured potentials are slightly lower, within the range of 160 ~ 240 mV (SHE). These are in agreement with the potential (above 250 mV, SHE) in a neutral aerated sodium chloride solution given by Eklund (132).

The observations in this investigation clearly showed the process of dissolution of MnS, as discussed in Section 5.3.3.1 and 5.3.3.2.
Fig. 5.51 Potential-Time diagram of Stainless steel 316 in 3.5% NaCl solution

3.5% NaCl solution
- pH 7
- pH 5
In the case of pH = 5 or 7, it is clear from Fig 5.50 that MnS cannot exist at potentials higher than -100 mV. Since the potential of the passive stainless steel surface is considerably higher (160 ~ 290 mV), the MnS inclusions should tend to dissolve. The following mechanism is suggested for the dissolution of MnS when polarised in a positive direction in a sodium chloride solution:

(1) Chloride ions adsorb on surface of MnS, shown in Fig 5.26 c. and Fig 5.29;

(2) The oxidation of MnS takes place at the interface between solution and MnS inclusion. The following reactions may be possible depending on the potential:

\[
\begin{align*}
\text{MnS} + 4\text{H}_2\text{O} &= \text{Mn}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e}^- \quad [4] \\
\text{MnS} + 3\text{H}_2\text{O} &= \text{Mn}^{2+} + \text{HSO}_3^- + 5\text{H}^+ + 6\text{e}^- \quad [*] \\
\end{align*}
\]

(3) The anodic dissolution of MnS will decrease the pH at the surface or in crevices surrounding the inclusion:

(4) The surface concentration of adsorbed Cl\textsuperscript{−} prevents accumulation of the sulphur-containing ions and these ions will tend to diffuse to the area surrounding the inclusions:

(5) It is considered possible that with the lowered pH, sulphur will be precipitated from the sulphur-containing ions by reaction at the cathode

\[
\begin{align*}
\text{SO}_4^{2-} + 8\text{H}^+ + 6\text{e}^- &= \text{S} + 4\text{H}_2\text{O} \quad [1] \\
\text{HSO}_3^- + 5\text{H}^+ + 4\text{e}^- &= \text{S} + 3\text{H}_2\text{O} \quad [**] \\
\end{align*}
\]

This would explain why the sulphur ring appeared, surrounding the inclusion group as shown in Fig 5.38-40, and Fig 5.43-44, which were taken

[4] and [**] These reactions were not included in Eklund's reaction scheme.
from the case of pH = 5. When pH = 7, the extent of acidification of solution in the local region should be lower compared with that of pH = 5, and thus the spread of sulphur would become apparent only in the latter stage of the exposure as was observed.

(6) As the dissolution and consumption of MnS become complete the concentration gradient of the sulphur-containing ions will decrease. In agreement with this, the sulphur Auger maps showed an increase in the intensity of the sulphur ring when the exposure time increased from 15 to 35 minutes followed by a decrease of contrast when the exposure time was increased to 80 minutes. Fig 5.38-41.

The dissolution of MnS at the boundary will expose the matrix metal to the solution. When the pH decreases by the dissolution of MnS in this local region the passivation of the exposed metal is difficult. At a certain moment metal atoms from the metal lattice will enter the solution. For metal iron, only one anodic reaction occurs during pitting:

\[ \text{Fe} = \text{Fe}^{2+} + 2\text{e}^- \]

The hydrolysis of metal ions will further decrease the pH in this region. This process of metal dissolution will enhance the attack on MnS by the mechanism proposed above and also enhance the cathodic potential of the surrounding region, greatly facilitating the reduction of sulphur-containing ions to sulphur.

As the dissolution of metal begins the potential on the surface of bare metal will drop drastically. Also it is possible that the decrease of both pH and potential will allow the following reactions to take place at the anode:
\[
\text{MnS} + 2\text{H}^+ = \text{Mn}^{2+} + \text{H}_2\text{S} \quad [6]
\]
\[
\text{H}_2\text{S} = \text{S} + 2\text{H}^+ + 2\text{e}^- \quad [2]
\]

Eklund (132) calculated the equilibrium potential-concentration diagram for the MnS-H\text{2}O-Cl\text{−} system at a total concentration of 0.1 mole/litre for SO\text{4}^{2−}, Cl\text{−}, and Mn\text{2}+. The stability ranges for the solid phases are also shown in his diagram. It is shown that Sulphur is a stable solid phase in the potential range of -100 - 300 mV (SHE) and he considered that the final product on the surface of inclusion group would be sulphur.

However it seems unlikely that elemental sulphur would diffuse to give the clear ring shown in the figures. It thus seems that at least part of the MnS dissolution occurs by means of reaction [4] or [6]. The active sulphur-containing ion being then reduced at the cathodic area surrounding the inclusions.

In order to identify the sulphur chemical states an attempt has been made to find such information by smoothing and differentiating the Auger spectra recorded from different stages and areas and observing the positions of peak and valley on these differential spectra. Fig 5.52 shows an example of those differential spectra. Unfortunately, the data did not show distinct difference in the peak position. The probable reasons are:

1. A small primary beam current has been used when the direct spectra were recorded, and many performances of the smoothing operation conceals any change of position which might have occurred.

2. The retard ratio of CRR 2 was used for the acquisition of Auger spectra, which means the pass energy was ~ 76 eV for the energy of Auger sulphur peak (L\text{_{2,3}VV}, ~152 eV), the energy resolution thus was not good enough to obtain chemical information.
Fig 5.52 An example of differential spectra deduced from direct spectra
The Auger transition of $S, L_{23}VV$ includes the valence band, the natural peak width is so broad as to obscure chemical state information. The use of a high energy Auger peak ($KL_{2}L_{3}$) may give such chemical state information.

It is quite clear that during the initiation of pitting both the MnS and matrix of steel at the boundary act as anode, whilst the passive film on the stainless steel act as cathode on which the following reactions might take place:

$$O_2 + 4H^+ + 4e^- = 2H_2O$$

$$HSO_3^- + 5H^+ + 4e^- = S + 3H_2O$$

Once the dissolution of MnS takes place, virgin metal is exposed to the environment. Since the electronic conductivity of the sulphide is lower then that of the metal matrix, the dissolution takes place preferentially at the boundary between the sulphide and the matrix. Therefore a small crevice will develop, which may be considered as crevice corrosion on a micro scale. One side of this crevice is the sulphide inclusion and the other side is the matrix. As mentioned above, after the dissolution of MnS, the pH decreases in this local region, thus the passivation of the exposed metal will be difficult on the wall of metal matrix. In the acid condition of pH = 5, it is probable that the rate of the dissolution of metal iron from the wall of micropit is greater than that of diffusion of the outgoing iron ions, the concentration of Fe ions in the micropit will higher then that on the passive surface. The dissolved metal ions, e.g. Fe$^{2+}$ may form hydroxides of iron and the precipitation FeOOH. Evidence that this does occur is shown by the enrichment of oxygen and iron seen in the Auger maps at the site of MnS inclusion when compared with the surrounding area, see Fig 5.38-41, 5.44. Confirmation that this is a
surface deposit is found in the X-ray maps of iron (Fig 5.35-36) which still showed that the intensity of iron on the matrix of stainless steel is higher than that on the inclusion group, because the X-ray analyses give the bulk (μm) information. The pH decrease associated with the dissolution of metal will be enhanced by the presence of a product sealing the crevice. Thus the observed precipitation of a cap of FeOOH covering crevice and inclusion exerts a profound effect.

Further, with the presence of microcrevices pitting can also be perpetuated by a crevice corrosion mechanism. This sequence of events results in an autocatalytic process.

Fig 5.53 shows schematically the picture discussed above.

Fig 5.53 Schematic diagram for initiation of pit at the site of MnS inclusion
On the Pourbaix diagram for iron (224), the reaction $\text{Fe} \rightarrow \text{Fe}^{2+}$ starts at a pH just less than 7 for the case of $E' = 0$. For the present range of potential and pH = 9, the potential-pH diagram for the Fe-H$_2$O system shows a passivation region. So in the experiment for pH = 9, although MnS dissolved away in the early stage of immersion, the Auger Fe maps do not show the enrichment of Fe ions on the surface of inclusion group. The signal contrast between the surface on the inclusions and the surrounding area on these maps do not show any obvious change.

When pH = 9, the early dissolution of MnS will form the oxide of manganese at the rest potential of stainless steel 316. The presence of the oxide of Mn will limit the further dissolution of MnS which is confirmed by the X-ray analyses shown in Fig 5.46.

It is suggested from above discussion that the initiation of pits on the site of inclusion of stainless steel 316 is the combination of several processes: the adsorption of the aggressive Cl$^-$ ions on the site of inclusion, the dissolution of MnS, the acidification in the microarea and followed by the dissolution of metal from the micro-region adjacent to the inclusions. Once the microcrevice forms, the mechanism for the crevice corrosion is of importance. The pH value of sodium chloride solution affects the rate of pit initiation by changing the equilibrium of system.

It is uncertain from the present observation, however, whether or not the sulphur precipitated on the surrounding area of inclusion group will contaminate the passive film and promote the propagation of pitting. The importance of sulphur in the electrochemical dissolution of nickel has been illustrated by Oudar and Marcus (228). The present work demonstrates how
sulphur is able to contaminate a region of the passive film surrounding inclusions. As shown in Fig 5.29, long exposures finally lead to chloride accumulation in the area of sulphur adsorption and this may represent the onset of general corrosive attack of the contaminated metal.
Chapter 6

Conclusions

The primary aim of this investigation was the study of the behaviour of inclusions in stainless steel in relation to that of the surrounding oxide film. To achieve this samples of a commercial stainless steel have been closely monitored during each stage of transfer from a vacuum-clean metallic surface to air and on to immersion in a chloride solution.

The changes occurring in the film have been followed (a) electrochemically, (b) by conventional angular resolved XPS, and (c) by a new use and interpretation of the background associated with photoelectron peaks.

This study has been correlated with the observation of inclusions by AES during repeated exposure to aqueous solutions. As a result of these two studies it can been seen that corrosive attack of the inclusion and release of sulphur can occur within the time taken for the film to transform from air to aqueous in character. This is especially true for acidic solutions. The sulphur compounds may become trapped as a result of the restructuring of the film or as a result of cathodic potentials set up by the initial pitting or crevice attack at the inclusion.

In the following pages, some specific conclusions arising from the investigation are given and discussed.

(1) The energy loss structure of photoelectron peak can be used to provide extra information relating to the layer sequences of surface elements.
In this work, the energy loss tail height, the slope of post-peak, and slope of base line have been shown to yield additional information on the depth distribution of iron and chromium in the near surface region of an Fe-Cr alloy, as a result of annealing in the spectrometer vacuum or oxidation followed by vacuum annealing.

Experimental observation and curve fitting of Cr and Fe spectra showed that the energy loss tail height and the slope of post-peak of the iron peak increases with the effective thickness of the Cr$_2$O$_3$-rich overlayer.

The variation in the slope of the base lines of the Cr and Fe peaks relates to the enrichment or otherwise of Cr and Fe in the oxide overlayer. The model is confirmed by the angular resolved XPS measurements and the argon-etch depth profile.

The same methods have been used to give such additional in-depth information on the composition of passive films formed in air and aqueous NaCl solution on stainless steel 316.

(2) The study on the pitting initiation shows that surface preparation is a key factor if the initial reaction with the electrolyte is to be observed.

The role of inclusions as initiators of pitting corrosion has been studied from the very inception of attack. However comparison of AES and EDX images on the probed surface shows a highly disturbed contamination layer to cover the inclusion. This contamination layer had to be removed by ion etching. Detailed observations have been taken from separate MnS inclusions and mixture of MnS and multi-element oxide particles.
(3) In neutral sodium chloride solution, X-ray and Auger electron analyses show that corrosive attack starts on MnS inclusion proper.

Attack occurs especially on the MnS in the crevice at the periphery of the multi-element oxide inclusion. Chloride ions cluster at the surface of MnS as well as oxide inclusions. Initially the concentration of Cl⁻ on oxide was even greater than that on sulphide particles. However, the corrosive attack on MnS become more severe on further exposure, and pits formed and deepened, particularly in the inclusion crevice.

The rate of anodic dissolution of metal in the microcrevices is accelerated by the decrease of pH in the solution of both bulk and micro-region of microcrevice. This is illustrated by the comparison of Auger and X-ray maps recorded from the specimens immersed in various pH solutions.

(4) During exposure, the sulphur spread to the whole surface of the inclusion group and the area surrounding the inclusions.

For the exposure in the solution of pH = 5, the Auger maps showed the bright sulphur ring to surround the inclusion group, which became stronger as the exposure increased, while the contrast reduced as the concentration gradient of sulphur-containing ions decreased on further exposure.

(5) During the exposure, the iron dissolved from the matrix side of microcrevice and formed hydroxides of iron and precipitates of FeOOH.

This is shown on the Auger maps by the enrichment of Fe and O on the surface of inclusion group. It may have formed a cap to retain corrosion solutions within the crevice.

The addition of OH⁻ ions, as inhibitors, slowed down the corrosion reactions. The results for pH = 9, have shown that the anodic dissolution
of MnS was inhibited by OH\textsuperscript{-} in the latter stage of exposure. The Fe Auger maps do not show the obvious change of intensity contrast as the exposure.

(6) When exposed in the 3.5% NaCl solutions, the behaviour of MnS and oxide inclusions is different.

The dissolution of the MnS inclusions takes place in all cases of pH = 5, 7, and 9. The rate depends the pH value of solutions. The lower the pH value, the greater the rate of the dissolution. The multielement oxide inclusions do not dissolve during the exposure in the 3.5% NaCl solutions.

It is suggested from this investigation that the initiation of pit on the site of inclusion of stainless steel 316 is the comprehensive effect of several processes including the adsorption of Cl\textsuperscript{-}, the dissolution of MnS, followed dissolution of bare metal from the matrix wall of microcrevices, and the acidification arising therefrom in these microareas and the simultaneous changes in the oxide film on the surrounding area. Once the microcrevice forms, the mechanism for the crevice corrosion plays an important role in the pitting corrosion.
1. L.L. Shreir, 1.1A Appendix in 'Corrosion', Eds L.L. Shreir
   Newnes-Butterworths, London Boston, 1:16 (1976)
2. C.J.L. Booker, 1.2 in ibid, 1:22
3. T.P. Hoar, 1.5 in ibid, 1:114
   150, 81 (1944)
   89, 167 (1946) 93, 1 (1948)
   Chapter 7 (1960) First Supplementary Volume, Arnold, London.
9. H.H. Uhlig, Proceedings of the Third International Congress on
   also Corros. Sci. 7, 325 (1967)
11. L.L. Shreir, 1.6 in 'Corrosion' 1:130
12. J.B. Lumsden and R.W. Staehle, Surface Analysis Techniques for
    Metallurgical Applications, ASIM, STP 596, (1976)
15. Ingemer Olefjord and Bengt-Olof-Elfstrom, Corrosion, NACE.
    38, 46 (1982)
    17, 209 (1977)
    Moscow, 396 (1966)
    38, 54 (1974)


23. J. E. Truman, 3.3 in 'Corrosion' 3: 31

24. Y. M. Kolotyrkin, Corrosion 19, 261t-268t (1963)


33. J. M. Kolotyrkin, Corrosion 19, 261 (1963)

34. N. Tomashow, G. Chernova and O. Marcova, Corrosion 20, 166t (1964)


37. R. J. Brigham, Corrosion 28, 177 (1972)

38. R. J. Brigham and E. W. Tozer, Corrosion 29, 33 (1972)


42. D. A. Stout, J. B. Lumsden and R. W. Staehle, Corrosion 35, 141-146 (1979)


47. V.D. Scott, Phil. Mag. 31(2) 331-338 (1975)
51. A. Bruchmann, R. Emmerlich and S. Mrowec, Oxid. Met. 5(2) 137-147 (1972)
52. J.E. Castle and M.R. Hunt, Corros. Sci. 16(3) 137-144 (1976)
60. J. Moreau, Comptes Rendus 236, 85 (1953)
67. J.E. Truman, K.R. Pirt, Corrs. Sci. 16(2) 103-108 (1976)
83. L. L. Shreir, 1.1 in 'Corrosion' 1:3 (1976)
84. R. P. M. Procter, 1.3 in 'Corrosion' 1:33 (1976)
86. M. Pourbaix, Corrosion 26, 431-438 (1970)
87. T. Suzuki and Y. Kitamura, Corrosion 28, 1-6 (1972)
89. W. Schwenk, Corrosion 20, 129t-139t (1964)
97. T. Suzuki and Y. Kitamura, Corrosion 28, 1-6 (1972)


100. Y. M. Kolotyrkin, Corrosion 19, 261t-268t (1963)

101. H. H. Uhlig and J. Gilman, Corrosion 19 261t (1963)

102. Y. Kolotyrkin, Corrosion 19, 261t (1963)


112. B. Kabanov, R. Burstein and A. Frumkin in ibid, 259-269


114. J. Van Muylder, M. Pourbaix and P. Van Lear in Rapport Technique No 127 CEBELCOR, Brussels. (1965)


121. Z. Szklarska-Smialowska, Corrosion 28, 338 (1972)
125. B. E. Wilde and J. S. Armijo, Corrosion 23, 208 (1967)
127. H. H. Uhlig, Trans. AIME 140, 441 (1940)
129. N. D. Greene and M. G. Fontana, Corrosion 15, 25 (1959)
134. A. R. Daud, Ph. D. Thesis, University of Surrey
138. H. Hertz, Ann. Physik. 31, 983 (1887)
139. H. R. Robinson and W. F. Rawlinson, Phil. Mag. 28, 277 (1914)
140. E. Rutherford, Phil. Mag. 28, 305 (1914)
141. K. Siegbahn, ed. Beta and Gamma-Ray Spectroscopy, North Holland, Amsterdam (1957), revised 1965


144. T. A. Carlson, Surface and Interface Anal. 4, 125 (1982)


170. P. Auger, J. Phys. Radium 6, 205 (1925)


177. S. Hofmann, Chapter 4 in Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, 141-179 (1983)


188. P. Sigmund, Phys. Rev. 184, 383 (1969)
196. Work carried out by J. F. Watts, University of Surrey, Reported in ref. 152
198. H. H. Andersen, Appl. Phys. 18, 131 (1979)
199. W. O. Hofer and V. Littmark, Phys. Lett. 71, 6 (1979)
200. S. Hofmann and A. Zalar, Thin Films, 60, 201 (1979)
204. C. S. Fadley, Prog. Sol. St Chem. 11, 265 (1976)
211. S. Tougaard, Surface Science 162, 875 (1985)

212. S. Tougaard, Surface Science 172, L503 (1986)


216. S. A. Richardson, I. A. Talib and J. E. Castle
Quantitative use of the energy loss tail on photoelectron peaks


218. S. J. B. Reed, Electron Microprobe Analysis (1975)


SEM Inc. AMF O’Hare (Chicago), IL60666 USA.


222. J. E. Castle and J. H. Qiu
To be published


227. Z. Szklarska-Smialowska, Corrosion-Nace, Vol.28, 10, (1972)

The combination of Auger electron and X-ray maps obtained from a SEM shows the surface chemistry of an inclusion group in 316 steel, relative to the bulk composition, before and after exposure to sodium chloride solution. Work of this type enables the role of inclusions as initiators of pitting corrosion to be studied from the very inception of attack.

Surface preparation is very important if the initial reaction with the electrolyte is to be observed and there are a number of difficult metallographic procedures. The sites of inclusions are first marked out on the highly polished surface using microhardness indentations under the optical microscope. The inclusions have poor contrast in the SEM and they must be located within the boundary of the indentations by X-ray mapping. A typical map in sulphur radiation is illustrated in Plate 1 (upper left quadrant). At this stage the Auger map (upper right) of the surface composition to a depth of 100 nm is very indistinct because of contamination from the polishing process. The Beilby layer is therefore removed in stages using the Auger signal to control the ion etching process until the sulphur Auger signal has the same clarity as that of the bulk. The lower quadrants in Plate 1 give the Auger maps after the removal of 1 and 6 nm respectively. These maps, although being used in a routine way, are undertaken with a screen magnification of 6400x and are good examples of high resolution Auger microscopy in their own right.

Plate 2 reveals the overall shape of an inclusion group by the drop in iron Auger signal. Plate 3 is a three-element X-ray map showing how sulphide ions (light blue) are released by corrosive attack on sulphides in the crevices at the periphery of the chromium oxide inclusion and diffuse into its porous interior. Plates 5 and 6 are Auger maps of sulphur and chlorine respectively showing that chloride ions cluster at the surface of the oxide inclusion whilst attack on the exposed surface of the sulphide is less severe.
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